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Heterogeneous Equilibria Between Aqueous
and Metallic Solutions.

The Interaction of Mixed Salt Solutions
and Liquid Amalgams.

A Study of the Ionization Relations of Sodium
and Strontium Chlorides in Mixtures

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AND METALLIC SOLUTIONS.
THE INTERACTION OF MIXED SALT SOLUTIONS
AND LIQUID AMALGAMS.
A STUDY OF THE IONIZATION RELATIONS OF SODIUM
AND STRONTIUM CHLORIDES IN MIXTURES.

BY

SILAS ALONZO BRALEY

A. B. Morningside College, 1913
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THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY Silas Alonzo Braley

ENTITLED Heterogeneous Equilibria between Aqueous and Metallic
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Amalgams. A Study of the Ionization Relations of Sodium and
Strontium Chlorides in Mixtures.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF Doctor of Philosophy

G. W. P. Smith

In Charge of Thesis

W. A. Hayes

Head of Department

Recommendation concurred in:*

Richard C. Tolman

F. R. Watson

Aug. T. Kneipp

Committee

on

Final Examination*

*Required for doctor's degree but not for master's.

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A handwritten signature in cursive script, reading "S. A. Braley". The signature is written in dark ink and is positioned to the right of the main text block.



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I. INTRODUCTION.

1. Purpose of the investigation:- In connection with the conflicting values for the relative ionization of salts in mixtures, a series of investigations is being carried out in this laboratory with the object of studying by an independent method the ionic relationships which exist in mixed salt solutions. This investigation is the fourth of the series and is based upon the equilibrium found to exist between sodium and strontium salts and the liquid amalgams. The method used is that originally developed by G. McP. Smith. (1)

2. Principles relating to the ionization of salts in mixtures:- Calculations from conductance data indicate that in general salts of the same ionic type are ionized to the same extent. (2) From the work of MacGregor, Archibald, McIntosh and McKay (3) the conclusion has been drawn that the conductance of a mixture of salts with a common ion corresponds to the value calculated on the assumption that the degree of ionization of each salt in the mixture is equal to that which it has when alone present in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the solution. (4) G. M. J. McKay (5) has later shown by transference experiments on solutions of KCl and K_2SO_4 that in solutions 0.2009 N with respect to each salt the specific conductance

of the KCl is 2 % lower and that of the K_2SO_4 is 5.2 % higher than the above principle would predict. But nevertheless he notes that the measured conductance of the solution does not differ by more than 1 % from that calculated on the assumption that the principle holds. He therefore concludes that the principle of the ionization of salts in mixtures is subject to serious inaccuracy especially in the case of salts of two different types such as studied. C. Sandonnini (6) has given experimental evidence showing that the measured conductivity of a mixture of a uni-valent and a uni-bivalent salt differs markedly from the value obtained by adding the measured conductivities of the individual salts. G. McP. Smith and T. R. Ball (7) have shown by the method used in this investigation that in mixed sodium and potassium chloride and sulphate solutions, containing the alkali salts in equivalent quantities, the io-fraction of the potassium is in all cases less than that of the sodium, although from the conductivity data and the principles of ionization as stated above it should be greater.

Sherrill (8) has studied by conductance methods the ionization of salts without a common ion in mixtures: he finds that if the concentrations of the ions of the salts in the mixtures are calculated according to the principle already referred to, - that $(A)(B)/(A_xB_y) = K(\sum i)^{2-n}$, then the calculated equivalent conductances of the mixtures agree with the observed values within about 1/2 % at 0.2 N and 1/4 % at 0.1 N. In this expression (A) and (B) are the ion concentrations, (A_xB_y) the concentration of the undissociated molecules, $\sum i$ the sum of the equivalent ion concentrations and "n" an empirical constant depending upon the nature of the salt, but falling in all cases between 1.40 and 1.55. Sherrill says, however, that the ionization relations of the di-ionic and tri- ionic salts may conceivably be determined by a different principle

instead of by the same principle as assumed, and that in this case the agreement which he obtained experimentally might be due to a compensation of errors.

It should be noted that up to the present time most of the principles arrived at have been based almost exclusively upon conductivity data, and that a disagreement exists between the values obtained by the conductivity methods and by other methods.

II.. THEORETICAL.

When a liquid sodium amalgam is placed in contact with a strontium salt solution, the sodium owing to its solution tension, tends to pass into the solution, and there results a difference of potential between the amalgam and the solution. The amalgam becomes negatively charged and attracts the positive ions of the solution, and, in case there are no impurities present, the strontium ions alone are discharged into the amalgam; and this action continues until the solution tension of the strontium in the amalgam assumes a value sufficiently great to prevent the further entrance of strontium from the solution. At this point equilibrium is of course established. This reaction has been shown by G. McP. Smith (2) to be reversible, so that if a liquid strontium amalgam is placed in contact with a sodium salt solution the opposite reaction will take place, with the final establishment of the same equilibrium. The reversible reaction may be written



In case a large excess of mercury is present, mercury may be eliminated from the equation and the mass law expression may be written as follows:

$$\frac{(\text{SrHg}_m)(\text{Na}^+)^2}{(\text{NaHg}_n)^2(\text{Sr}^{++})} = C_0 \quad (1)$$

But this expression is of no value unless we can determine either the ion-concentration ratio of the metals or the value of C_0 .

In a mixed salt solution, however, the concentration of the salts may readily be determined, and the ratio of these concentrations must be some function of the ion-concentration ratio; i.e.,

$$\frac{(\text{Na Salt})^2}{(\text{Sr Salt})} = n \frac{(\text{Na}^+)^2}{(\text{Sr}^{++})} \quad (2)$$

In which "n" is some unknown quantity, constant or otherwise. But if the salt solution is made infinitely dilute "n" of necessity must be equal to unity, since the salts will then be completely ionized. At infinite dilution then, the salt concentrations can be substituted for the ion concentrations, and we obtain the following expression:

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_o^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_o} = C_0 \quad (3)$$

in which the subscript "o" indicates infinite dilution of the salts. But at any other concentration "c" an expression may be written

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_c^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_c} = C_c \quad (4)$$

And, since the value of C_c will approach that of C_0 as the concentration approaches zero, it follows that the value of C_0 may be obtained by plotting the values of C_c determined in the case of a fixed salt-concentration ratio at several different salt concentrations, against the total salt concentrations, and extrapolating the curve to

infinite dilution.

Now, in the case of any given equilibrium mixture, it follows from the preceeding equations that

$$\frac{(\text{SrHg}_m)}{(\text{NaHg}_n)^2} = C_o \frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} \quad (5)$$

and that

$$\frac{(\text{SrHg}_m)}{(\text{NaHg}_n)^2} = C_c \frac{(\text{Sr Salt})_c}{(\text{Na Salt})_c^2} \quad (6)$$

But, providing a given total amalgam concentration is maintained, the ratio of the the amalgam concentrations at equilibrium is constant in the case of any given mixed sodium and strontium chloride solution. That is, in the case of each specific equilibrium mixture the relationship exists, that

$$C_o \frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} = C_c \frac{(\text{Sr Salt})_c}{(\text{Na Salt})_c^2} \quad (7)$$

or

$$\frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} = \frac{C_c (\text{Sr Salt})_c}{C_o (\text{Na Salt})_c^2} = a \quad (8)$$

If the concentrations be expressed in terms of mol-fractions

$$(\text{Sr}^{++}) + (\text{Na}^+) = 1 \quad \text{and} \quad (\text{Sr}^{++}) = 1 - (\text{Na}^+)$$

Substituting this value of (Sr^{++}) in equation (8), we obtain

$$\frac{1 - (\text{Na}^+)}{(\text{Na}^+)^2} = a \quad (9)$$

whence

$$(\text{Na}^+) = \frac{-1 \pm \sqrt{1 + 4a}}{2a} \quad (10)$$

in which "a" equals

$$\frac{C_c (\text{Sr Salt})_c}{C_o (\text{Na Salt})_c^2}$$

Therefore after having once determined the value of C_o it is possible to determine the ion-fraction of the metals in the solutions containing the salts at a fixed mol-fraction ratio and also in

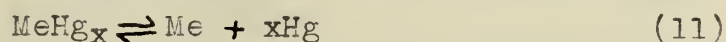
mixtures in which the salts are present in different mol-fraction ratios, for according to the mass law the same value of C_c will also hold in the latter case.

In the case of the system sodium-potassium, with the use of solutions of fixed composition and concentration, G. McP. Smith and T. R. Ball (7) have found that changes in the concentration of the amalgam lead to changes in the value of C_c . Now if in the mass law expression

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_c^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_c} = C_c$$

the concentrations of the salts are kept constant and the value of C_c is found to change with changing total amalgam concentration, then it follows of necessity that the ratios of the amalgam concentrations must also change in proportion. From this the conclusion may be drawn that the relative tendency of each metal to react is not proportional to its relative total concentration in the amalgam. Since the reacting tendency or solution tension of the amalgam is dependent upon its degree of dissociation into mercury and other free metallic atoms, and, since we are now in a position to determine the relative tendencies of the two metals to react, it should therefore be possible to determine in a relative manner the effect of concentration changes upon the degree of dissociation of either amalgam.

In any liquid amalgam the following equilibrium exists,



and the equilibrium expression may be represented by

$$\frac{(\text{Me})(\text{Hg})^x}{(\text{MeHg}_x)} = K \quad (12)$$

But since the solvent in which this equilibrium exists is mercury, and since in the case of the amalgams under consideration the degrees of dissociation are undoubtedly very small, the concentration of the mercury in the above expression may be neglected, and it then becomes,

$$\frac{(Me)}{(MeHg_x)} = K \quad (13)$$

Upon analysis of the equilibrium amalgam, the total equivalents, "y", of Me may be determined, and we have

$$Me + MeHg_x = y \quad (14)$$

By substituting the value of $MeHg_x$ from equation (14) into equation (13) it becomes

$$\frac{Me_1}{y_1 - Me_1} = K \quad (15)$$

at a given concentration, 1; at a second concentration, 2, it becomes

$$\frac{Me_2}{y_2 - Me_2} = K \quad (16)$$

and at a concentration "n" it becomes

$$\frac{Me_n}{y_n - Me_n} = K \quad (17)$$

Equating these expressions one to the other and solving for Me_1 , we obtain

$$Me_1 = \frac{y_1}{y_2} Me_2 = \frac{y_1}{y_3} Me_3 = \dots = \frac{y_1}{y_n} Me_n \quad (18)$$

or, if the degree of dissociation in the amalgam at concentration 1 be considered as unity, then at any concentration "n",

$$Me_n = \frac{y_n}{y_1} \quad (19)$$

From this equation, with the use of the analytical data obtained in equilibrium experiments carried out with mixed solutions of fixed composition and concentration, but with liquid amalgams of varying

total concentration, it is possible to calculate the proportional number of free atoms, existing at equilibrium, in the amalgams.

III. MATERIALS, APPARATUS AND METHOD OF EXPERIMENTATION.

1. Materials:- The decomposition of the amalgam by the water of the salt solution is catalyzed by dust particles on the surface of the mercury or by heavy metals contaminating the solution or the amalgam. The catalytic action of heavy metals is especially pronounced. Toward the latter part of the investigation it was necessary to prepare a fresh quantity of strontium chloride and this was purified from a fresh supply of the commercial salt by exactly the same procedure as that presently to be described. Upon using this purified salt there was a vigorous evolution of hydrogen, and in some cases the amalgams were entirely decomposed in a very short time. Other new materials such as water and mercury were then repurified, and still the action was the same. It was therefore evident that some material not removed by recrystallization was present in the strontium chloride, and for that reason a fresh quantity of the salt was prepared from high grade strontium carbonate and hydrochloric acid. After purification in the same way, by crystallization, the action of this salt was entirely normal. When dust particles contaminate the solution or the amalgam the action is quite different; it is then localized on the surface of the amalgam and may be stopped by removing the spot from which the action comes, or in many cases

the action will spontaneously cease, owing to the removal of the dust particle from the surface of the amalgam by the gas evolved. The apparent ease with which the decomposition of the amalgam is catalyzed makes it necessary to use only the purest of materials.

(a) Water:- The distilled water of the laboratory was successively distilled from alkaline potassium permanganate and dilute sulphuric acid as described by G. McP. Smith and T. R. Ball. (7)

(b) Sodium Chloride:- The commercial salt was twice precipitated ^{by} gaseous hydrogen chloride, each time filtered, and the last traces of mother liquor thrown out with a high speed electric centrifuge. It was finally dried on an electric hot-plate until the odor of HCl could no longer be detected. Just before using it was heated in the electric muffle for one hour at 750° to 800°.

(c) Strontium Chloride:- A good grade of commercial salt was first recrystallized from hot water containing hydrochloric acid. The mother liquor ^{was} removed as far as possible, first by filtration on the suction pump, and later by means of the centrifuge. A second crystallization was made from pure water and the mother liquor removed as before; after this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(d) Mercury:- Commercial mercury was filtered through a pin-hole filter, shaken with successive portions of potassium ^{dichromate} sulphuric acid solution, washed, passed through a column of mercurous nitrate in dilute nitric acid, again washed, dried, and finally distilled, all as described by G. McP. Smith and T. R. Ball. (7)

(e) Amalgams:- The amalgams were prepared by electrolysis as described by G. McP. Smith and H. C. Bennett. (10) The liquid stock amalgams were not made to conform to any particular concentra-

tion, but in most cases they were made rather concentrated; in all cases they were analyzed and diluted with mercury before using.

(f) Asbestos:- A very good grade of commercial asbestos was boiled for several hours with concentrated hydrochloric acid, after which the acid was filtered off and the asbestos treated a second time with a fresh portion of acid. The asbestos was then thoroughly washed, mixed into a soup with dilute nitric acid and preserved in a glass stoppered bottle.

(g) Apparatus:- A description of the apparatus used in this investigation will be found in the paper, already referred to, by G. McP. Smith and T. R. Ball; (7) no changes were found to be necessary, and therefore it will suffice to refer the reader to the original description.

(3) Method of experimentation:- (a) Solutions:- Separate solutions of sodium chloride and strontium chloride were made up with concentrations equal to the total concentration desired for the mixed salt solution. Then by mixing the two solutions in the proper volume proportions, it was possible to prepare solutions having the same total concentration and any salt-concentration ratio desired.

For the sodium chloride solution, the dried salt was weighed out in the calculated quantity, dissolved in water, transferred quantitatively to a volumetric flask, and diluted to the mark at 25°.

For the strontium chloride solution, a quantity of the hydrated salt was weighed out such as would give a solution slightly more concentrated than that desired. This amount was then dissolved in water, diluted to a convenient volume, and the normality determined by the Volhard volumetric method for chlorine. (11) This solution was then accurately diluted to the required normality.

(b) Equilibrium:- As it was desired in each run to start with

amalgams having as nearly as possible the same equivalent concentration, the analyzed stock amalgams were in each run diluted with mercury to the concentration desired. The mercury for dilution was weighed out on a small trip balance with an accuracy of 0.1 - 0.2 gram, and then placed in the reaction flask. Fifty cubic centimeters of the mixed salt solution were next added, and the whole balanced on the trip balance. A sufficient quantity of the stock amalgam was then added to give altogether about 4.7 milli-equivalents of the amalgamated metal. The flask was then placed in the thermostat. After shaking for fifteen minutes the solution was decanted from the amalgam, a fresh portion of the solution added, the flask again placed in the thermostat and shaken for fifteen minutes. When dilute solutions were used the amalgams were treated in the above manner with six successive portions of the solution, whereas for the more concentrated solutions not so many renewals were required to produce the required equilibrium. After decanting the last portion of the solution, the amalgams were washed and decomposed according to the procedure of G. McP. Smith and T. R. Ball. (7) Each run was made with six separate reaction mixtures.

(c) Treatment of the decomposition products:- The hydrochloric acid solution containing the sodium and strontium chlorides was quantitatively withdrawn from the mercury in the decomposition flask, evaporated to dryness on the steam bath to remove the excess of acid, and then analyzed for strontium and sodium. The mercury itself was dried and accurately weighed to 0.1 to 0.2 gram.

(d) Determination of sodium and strontium:- Several methods were tried for the determination of the sodium and strontium in the solution. It was found almost impossible to accurately weigh the mixed chlorides because of the hygroscopic nature of the anhydrous

strontium chloride. This fact made it necessary to weigh each of the two metals in some convenient form. The regular method of first precipitating the strontium as carbonate with subsequent precipitation as sulphate was excluded because of errors likely to be introduced in driving off the ammonium salts previous to the determination of the sodium. The method finally arrived at was as follows: The acid free mixed-chloride residue was dissolved in about fifty cubic centimeters of water, dilute sulphuric was added in slight excess and then a quantity of alcohol equal to the volume of the solution.

(12) This solution was allowed to stand for some time, usually over night. At the end of this time it was filtered through a Gooch filter, washed thoroughly with fifty percent alcohol containing a small amount of sulphuric acid, and finally with pure alcohol. The crucible containing the strontium sulphate was then dried in the electric oven and finally ignited in the electric muffle. For the ignition, the crucible was placed in the cold furnace, and the current turned on and allowed to run for one hour; at the end of this time the temperature was about 750° . The Gooch filter used had previously been dried and ignited under the same conditions.

The filtrate from the strontium sulphate was evaporated to a small volume, transferred to a weighed platinum dish, and evaporated to dryness. The sodium sulphate residue was very carefully heated until fumes of sulphur trioxide were no longer given off, and then fused.

To show the constancy in weight of the Gooch filters, six were prepared and ignited as above. After being weighed they were washed, dried and re-ignited. The difference in the weight was not greater than 0.5 milli-grams in but one case, in which it was 1.0

milli-gram. In the average determination of C_c , this greatest difference would cause an error of less than one percent.

IV. EXPERIMENTAL DATA.

The following tables contain the data that have been obtained in this investigation. The figures in the first column in each table refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth and fifth columns contain data, in grams, obtained in the analysis of the equilibrium amalgam; column six shows the concentration of the amalgam, at equilibrium, in total milli-equivalents of amalgamated metals per 10 grams of mercury, - as calculated from the data in columns three, four and five; columns seven and eight give the atomic fractions of the metals in the equilibrium amalgam, as calculated from columns three and four; column nine contains the value of the mass law expression

$$\frac{(\text{SrHg}_m)(\text{NaCl})_c^2}{(\text{NaHg}_n)^2(\text{SrCl}_2)_c} = C_c$$

in which (NaHg_n) and (SrHg_m) are the atomic fractions of the amalgamated metals from columns seven and eight, and (NaCl) and (SrCl_2) the respective mol-fractions in the salt solution.

(1) Effect of varying the concentration of the liquid amalgam:-

In the case of the sodium-potassium equilibrium, G. McP. Smith and

Table I

Showing the effect of varying the concentration of the liquid amalgam

Total Concentration 0.2 N.

NaCl: 1/2 SrCl₂

Temperature 25°.

No	start	Amal. at	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic fract- tions of amal- gamated metals		C _c	C _c Cor. to A milli-equivs per 10 gms Hg.
			Na ₂ SO ₄	SrSO ₄	Hg		Na	Sr		
1		Sr	.0695	.2808	28.98	1.399	.3436	.6564	7.41	A = 1.369
2		Sr	.0702	.3129	29.16	1.499	.3687	.6313	6.19	
3		Sr	.0506	.2043	20.56	1.426	.3907	.6093	5.32	
4		Na	.0593	.2197	24.84	1.296	.4111	.5889	4.54	
5		Na	.0700	.2515	29.23	1.277	.4016	.5984	4.95	
6		Na	.0616	.1918	26.59	1.116	.4525	.5475	3.57	
7		Sr	.0674	.3383	27.58	1.715	.3347	.6653	7.92	
8		Sr	.0656	.3058	26.82	1.585	.3569	.6431	6.73	
9		Sr	.0629	.3082	25.50	1.663	.3458	.6542	5.80	
10		Na	.0617	.2015	28.79	1.062	.4431	.5569	3.78	
11		Na	.0537	.1827	25.66	1.070	.4317	.5683	4.06	
12		Sr	.0583	.2976	27.00	1.504	.3363	.6637	7.84	
13		Sr	.0521	.2538	24.50	1.427	.3469	.6531	7.25	
14		Na	.0543	.2508	27.00	1.294	.3591	.6409	6.64	
15		Na	.0523	.2470	26.00	1.314	.3540	.6460	6.89	
16		Na	.0522	.2268	26.00	1.232	.3737	.6263	5.98	
17		Sr	.0527	.2623	23.50	1.557	.3367	.6633	7.82	
18		Sr	.0524	.2480	23.00	1.496	.3534	.6466	6.92	
19		Sr	.0575	.2735	25.00	1.515	.3523	.6477	6.97	
20		Na	.0568	.2563	28.00	1.283	.3643	.6357	6.40	
21		Na	.0440	.1809	21.50	1.204	.3863	.6137	5.50	
22		Na	.0479	.1943	23.50	1.183	.3906	.6094	5.34	
					Mean	1.369			6.08	6.05
23		Sr	.0737	.2352	46.39	0.775	.4477	.5523	3.67	A = 0.753
24		Sr	.0805	.2482	50.14	0.757	.4561	.5439	3.49	
25		Sr	.0727	.2110	50.34	0.659	.4712	.5288	3.18	
26		Na	.0761	.2155	50.12	0.682	.4726	.5274	3.15	
27		Na	.0794	.2341	50.60	0.724	.4672	.5328	3.33	
28		Na	.0740	.2174	50.19	0.678	.4660	.5340	3.35	
29		Sr	.0875*	.2520	51.70	(0.768)	.4731	.5269	(3.14)	(3.08)
30		Sr	.0815	.2448	49.50	0.772	.4626	.5374	3.35	3.27
31		Sr	.0910*	.2695	52.90	(0.801)	.4734	.5266	(3.21)	(2.98)
32		Na	.0849	.2566	54.90	0.727	.4613	.5387	3.38	3.50
33		Na	.0800	.2388	52.00	0.717	.4641	.5359	3.32	3.49
34		Na	.0652	.1697	44.00	(0.669)	.4986	.5014	(2.71)	(3.05)
					Mean	0.721			3.36	3.51
35		Sr	.1214	.2520	102.0	0.436	.5562	.4438	1.91	A = 0.390
36		Sr	.1242	.2540	102.0	0.444	.5605	.4395	1.87	
37		Sr	.1190	.2408	102.0	0.426	.5573	.4427	1.86	
38		Na	.1167	.2115	102.0	0.387	.5878	.4122	1.59	
39		Na	.1116	.2128	102.0	0.380	.5756	.4244	1.71	
40		Na	.1124	.2155	101.6	0.368	.5743	.4257	1.74	

(Continued on page 15)

Table I (cont)

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No	Amal. at start	Eq'm amalgam gave on analysis			Amalg. Conc. in milli-equvs. per 10 gms. Hg.	Atomic fract- tions of amal- gamated metals		C _c	C _c Cor. to A milli-equvs per 10 gms Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na	Sr		
41	Sr	.1150	.2446	101.0	0.424	.5486	.4514	2.00	1.84
42	Sr	.1170	.2371	101.8	0.417	.5598	.4402	1.88	1.76
43	Sr	.1083	.2260	95.5	0.419	.5536	.4464	1.94	1.81
44	Na	.0985	.1745	101.5	0.324	.5932	.4068	1.54	1.85
45	Na	.1079	.1914	102.5	0.351	.5972	.4028	1.51	1.68
46	Na	.1140	.2293	105.0	0.390	.5627	.4373	1.85	1.85
				Mean	0.394			1.78	1.76
									A = 0.225
47	Sr	.1442	.1903	194.0	0.217	.6621	.3379	1.03	1.07
48	Sr	.1560	.2160	217.0	0.209	.6511	.3489	1.12	1.23
49	Sr	.1442	.1909	202.0	0.203	.6614	.3386	1.04	1.15
50	Na	.1399	.1794	199.5	0.197	.6685	.3315	.991	1.13
51	Na	.1352	.1678	199.5	0.187	.6756	.3244	.950	1.14
52	Na	.1279	.1556	182.5	0.197	.6663	.3337	1.00	1.14
53	Sr	.1533	.2162	199.0	0.226	.6478	.3522	1.12	1.11
54	Sr	.1644	.2431	207.0	0.240	.6371	.3629	1.19	1.11
55	Sr	.1540	.2187	202.5	0.224	.6455	.3545	1.14	1.14
56	Na	.1264	.1432	193.0	0.173	.6953	.3047	.842	1.09
57	Na	.1298	.1541	198.0	0.177	.6854	.3146	.895	1.14
58	Na	.1175	.1278	194.5	0.157	.7149	.2851	.745	1.07
59	Sr	.1665	.2486	202.5	0.249	.6339	.3661	1.22	1.10
60	Sr	.1666	.2553	204.0	0.251	.6279	.3721	1.26	1.13
61	Sr	.1573	.2215	206.0	0.224	.6474	.3526	1.12	1.12
62	Na	.1430	.1870	204.0	0.199	.6635	.3365	1.02	1.15
63	Na	.1290	.1514	202.0	0.173	.6841	.3159	.902	1.17
64	Na	.1308	.1613	193.0	0.186	.6772	.3228	.941	1.14
				Mean	0.205			1.01	1.14
									A = 0.0935
65	Sr	.1537	.1035	397.0	0.083	.7936	.2064	.438	.494
66	Sr	.1649	.1218	392.5	0.093	.7779	.2221	.490	.493
67	Sr	.1769	.1510	406.0	(0.103)	.7519	.2481	(.586)	(.529)
68	Na	.1605	.1144	393.0	0.089	.7834	.2166	.472	.495
69	Na	.1557	.1035	396.0	0.084	.7957	.2043	.431	.482
70	Na	.1557	.1047	395.5	0.084	.7937	.2063	.438	.486
				Mean	0.086			.454	.490
									A = 0.043
71	Sr	.1893	.0866	796.5	0.045	.8498	.1502	.278	.265
72	Sr	.1985	.0926	793.5	0.048	.8473	.1527	.284	.255
73	Sr	.1925	.0826	804.0	0.045	.8576	.1424	.258	.247
74	Na	.1535	.0534	811.0	0.034	.8795	.1205	.208	.264
75	Na	.1402	.0489	802.0	0.031	.8812	.1188	.205	.280
76	Na	.1376	.0458	797.5	0.030	.8861	.1139	.194	.274
				Mean	0.039			.238	.263

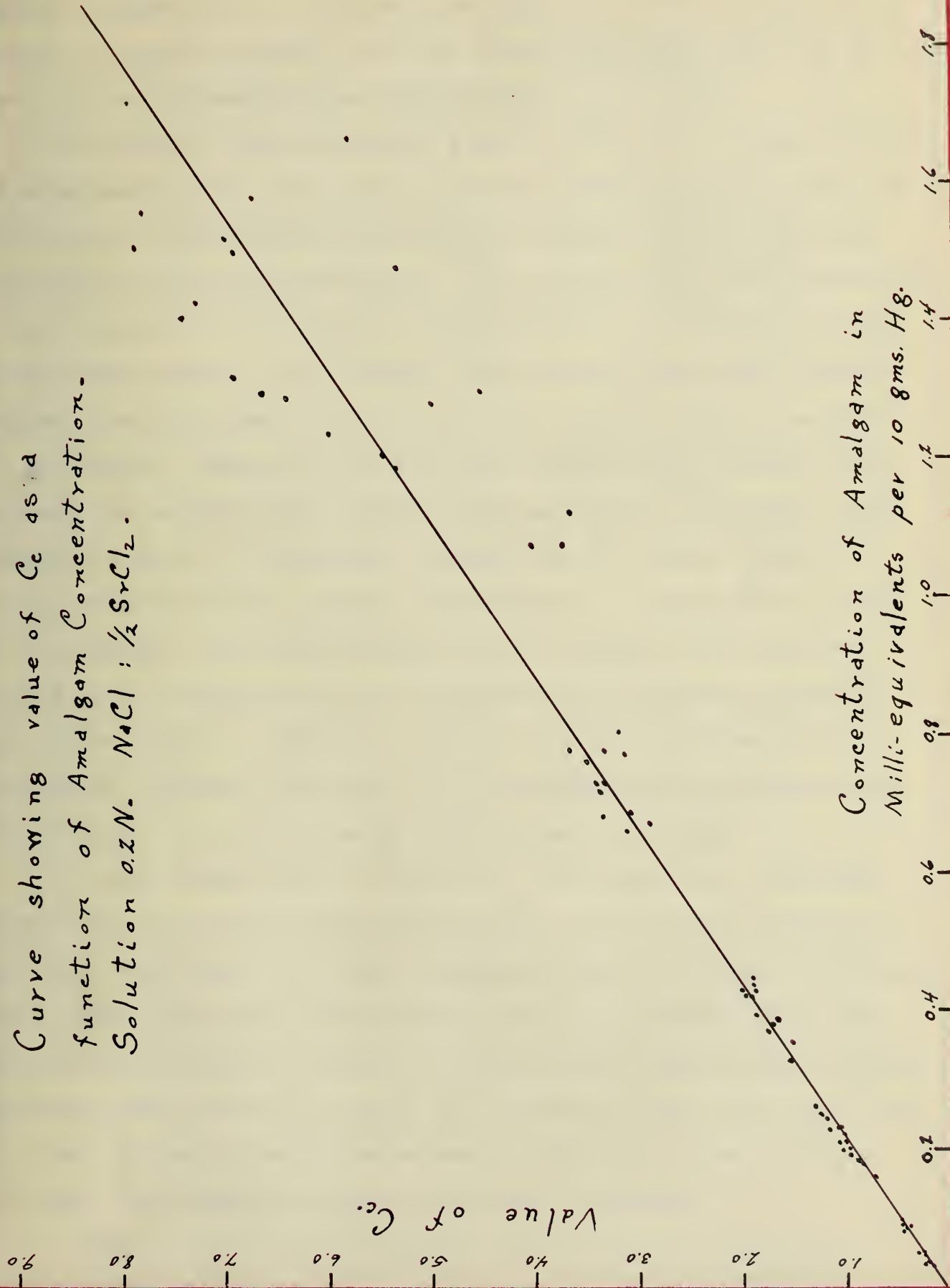
* Sodium Sulphate slightly contaminated.

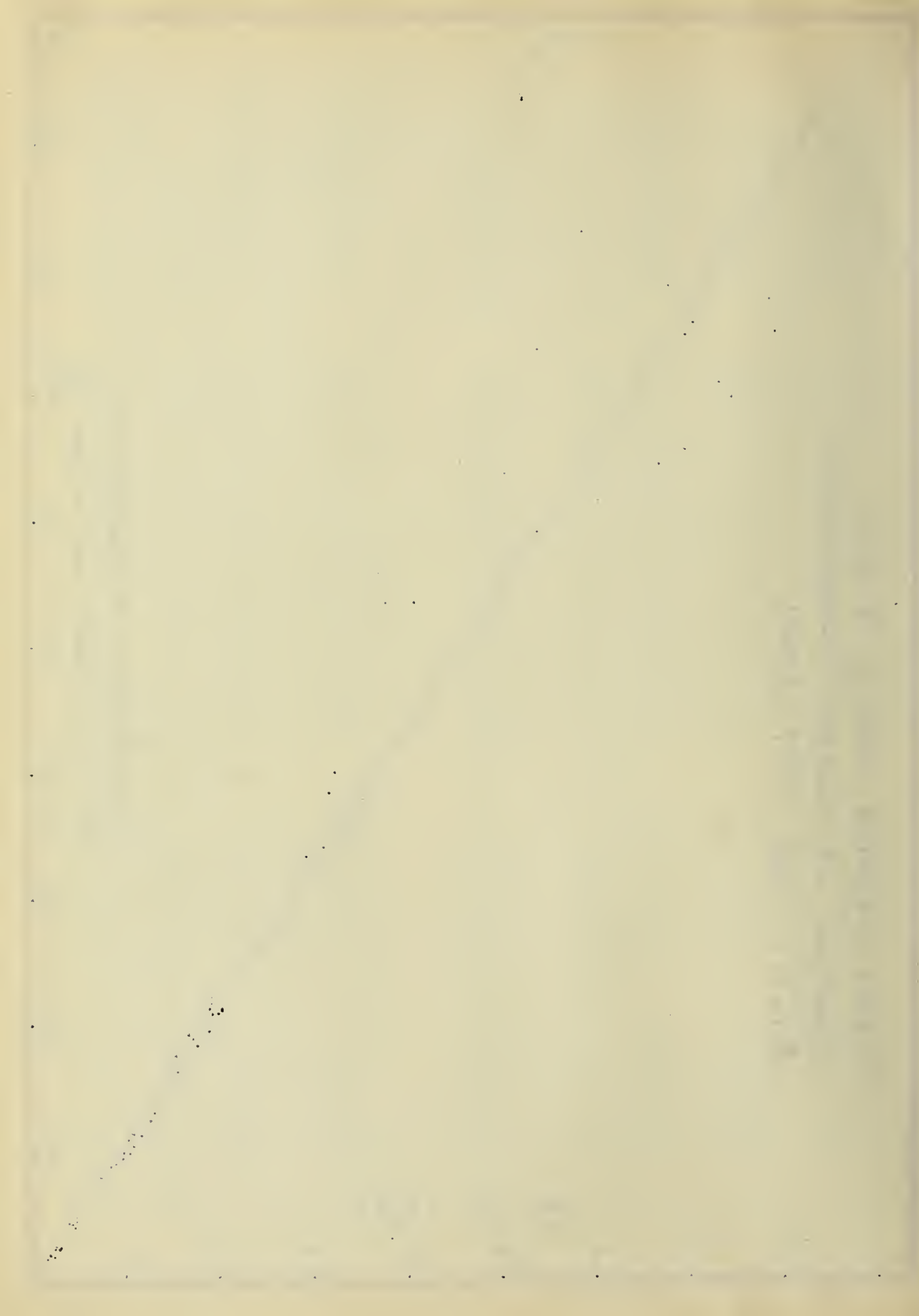
Fig. 1.

Curve showing value of C_c as a
function of Amalgam Concentration.
Solution 0.2N. $\text{NaCl} : \frac{1}{2} \text{SrCl}_2$.

Value of C_c .

Concentration of Amalgam in
Milli-equivalents per 10 gms. Hg.





T. R. Ball (7) have observed that changing the concentration of the liquid amalgam exerts a decided effect upon the value of C_c , and it therefore seemed advisable to first investigate this effect in the case of the sodium-strontium equilibrium.

The data for this study are given in Table I. In this series of experiments, with solutions of a total normality of 0.2, the concentration of the original amalgam was decreased one-half for each successive set of determinations. It was noted that the mean values of C_c obtained in the different sets decrease in direct proportion to the mean values of the amalgam concentration, but that the individual determinations at any one initial concentration of amalgam do not check. However, upon plotting the individual values of C_c against the corresponding amalgam concentrations, a straight line, shown in Fig. 1, was obtained, showing that the value of C_c is a linear function of the amalgam concentration. Since this is true it is possible, by a simple proportion, to correct the individual values of C_c to some definite concentration of amalgam and obtain concordant values. Therefore column ten has been added to the tables and contains the value of C_c corrected to some concentration "A" in total milli-equivalents per 10 grams of mercury.

G. McP. Smith and T. R. Ball (7) also found that when highly concentrated sodium or potassium amalgams were used the values of C_c were not concordant. In this connection attention should be called to the wide variation in the values of C_c in the first twenty-two experiments in Table I, where very concentrated sodium and strontium amalgams were used and in which the corrected values vary from 7.25 to 4.38; in the succeeding experiments with more and more dilute amalgams, the values of C_c are much more concordant.

Tables II, III and IV contain data showing the effect of

Table II

Total Concentration 0.4 N

NaCl : 1/2 SrCl₂

Temperature 25°

No.	Amal. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli- equivs. per 10 gms. Hg.	Atomic frac- tions of amal- gamated metals		C _c	C _c Cor. to A milli- equivs per 10 gms.Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na.	Sr.		
1.	Sr	.1115	.2390	50.3	0.830	.5469	.4531	2.03	A = 0.753 1.79
2.	Sr	.1115	.2402	50.0	0.837	.5455	.4545	2.04	1.75
3.	Sr	.1115	.2395	49.7	0.843	.5463	.4537	2.03	1.77
4.	Na	.1256	.2763	51.0	0.853	.5403	.4597	2.10	1.68
5.	Na	.1190	.2525	50.0	0.885	.5496	.4504	1.99	1.65
6.	Na	.1236	.2770	50.5	0.942	.5359	.4641	2.16	1.68
				Mean	0.865			2.06	1.72
7.	Sr	.1471	.1755	100.5	0.396	.6845	.3155	.900	A = 0.390 .886
8.	Sr	.1526	.1955	100.0	0.428	.6688	.3312	.990	.902
9.	Sr	.1479	.1802	100.5	0.404	.6776	.3224	.938	.905
10.	Na	.1480	.1774	101.5	0.396	.6833	.3167	.909	.895
11.	Na	.1435	.1695	100.5	0.385	.6865	.3135	.889	.901
12.	Na	.1410	.1789	98.2	0.384	.6896	.3104	.872	.886
				Mean	0.399			.916	.896
13.	Sr	.2119	.1814	200.0	0.248	.7512	.2488	.589	A = 0.225 .534
14.	Sr	.2151	.1893	202.1	0.252	.7461	.2539	.610	.545
15.	Sr	.2077	.1807	198.8	0.246	.7482	.2518	.601	.549
16.	Na	.1887	.1432	199.7	0.211	.7731	.2269	.506	.539
17.	Na	.1890	.1431	200.4	0.206	.7734	.2266	.506	.554
18.	Na	.1870	.1417	200.0	0.209	.7735	.2265	.506	.545
				Mean	0.228			.553	.546
19.	Sr	.2226	.0980	400.0	0.0950	.8546	.1454	.266	A = 0.0935 .237
20.	Sr	.2091	.0872	400.0	(0.0937)	.8739	.1261	(.221)	(.221)
21.	Sr	.2152	.1005	398.0	0.1040	.8471	.1529	.285	.257
22.	Na	.1593	.0558	377.0	0.0756	.8811	.1189	.205	.253
23.	Na	.1840	.0776	381.5	0.0900	.8599	.1401	.253	.258
24.	Na	.2065	.0915	393.0	0.0995	.8533	.1467	.269	.252
				Mean	0.0928			.256	.251

Temperature 25°

No	Amal. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	C _c Cor. To A milli-equivs per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg	Na.	Sr.	A = 0.753		
1.	Sr	.1520	.1900	50.0	0.842	.6741	.3259	.958	.857
2.	Sr	.1527	.1910	49.0	0.827	.6739	.3261	.959	.828
3.	Sr				Lost				
4.	Na	.1486	.1715	51.0	0.777	.6914	.3086	.862	.836
5.	Na	.1365	.1610	47.0	0.783	.6873	.3127	.885	.850
6.	Na	.1436	.1685	52.0	(0.742)	.6879	.3121	(.885)	(.898)
				Mean	0.807			.916	.843
									A = 0.390
7.	Sr	.1843	.1359	100.0	0.408	.7782	.2218	.489	.468
8.	Sr	.1935	.1545	102.5	0.430	.7642	.2358	.539	.489
9.	Sr	.1855	.1315	100.0	0.404	.7848	.2152	.467	.450
10.	Na	.1751	.1150	100.0	0.372	.7975	.2025	.425	.446
11.	Na	.1700	.1137	100.5	0.361	.7945	.2055	.435	.469
12.	Na	.1741	.1149	99.7	0.371	.7969	.2031	.427	.449
				Mean	0.391			.463	.462
									A = 0.225
13.	Sr	.2270	.1060	198.4	0.219	.8471	.1529	.285	.292
14.	Sr	.2315	.1063	200.5	0.220	.8492	.1508	.279	.285
15.	Sr	.2292	.1078	200.3	0.220	.8461	.1539	.287	.294
16.	Na	.2247	.1055	200.0	0.206	.8467	.1533	.285	.298
17.	Na	.2288	.1073	200.0	0.220	.8465	.1535	.286	.293
18.	Na	.2288	.1100	200.2	0.220	.8434	.1566	.293	.299
19.	Sr	.2290	.1012	200.0	0.216	.8540	.1460	.268	.288
20.	Sr	.2301	.1003	200.4	0.216	.8558	.1442	.263	.274
21.	Sr	.2278	.1000	200.3	0.215	.8548	.1452	.266	.279
22.	Na	.2288	.1057	196.4	0.223	.8485	.1515	.281	.284
23.	Na	.2289	.1064	196.4	0.223	.8477	.1523	.283	.285
24.	Na	.2340	.0994	196.4	(0.224)	.8594	.1406	(.256)	(.257)
25.	Sr	.2313	.1042	201.0	0.219	.8542	.1458	.267	.274
26.	Sr	.2330	.1027	199.5	0.221	.8540	.1460	.268	.273
27.	Sr	.2263	.1005	200.1	0.214	.8535	.1465	.269	.282
28.	Na	.2342	.1022	200.8	0.220	.8559	.1441	.263	.269
29.	Na	.2248	.1112	201.5	(0.217)	.8398	.1602	(.304)	(.314)
30.	Na	.2326	.0985	201.0	0.217	.8593	.1407	.256	.263
				Mean	0.218			.275	.283
									A = 0.0935
31.	Sr	.2335	.0800	398.0	0.1045	.8832	.1168	.200	.178
32.	Sr	.2425	.0810	401.0	0.1071	.8856	.1144	.195	.169
33.	Sr	.2455	.0660	402.6	0.1073	.9059	.0941	.153	.137
34.	Na	.2316	.0635	401.0	0.0985	.9041	.0959	.157	.148
35.	Na	.2325	.0610	402.0	0.0979	.9079	.0921	.149	.142
36.	Na	.1803	.0350	392.7	0.0743	.9300	.0700	.108	.136
				Mean	0.0983			.160	.151

Table IV

Total Concentration 1.2 N.

NaCl : 1/2 SrCl₂

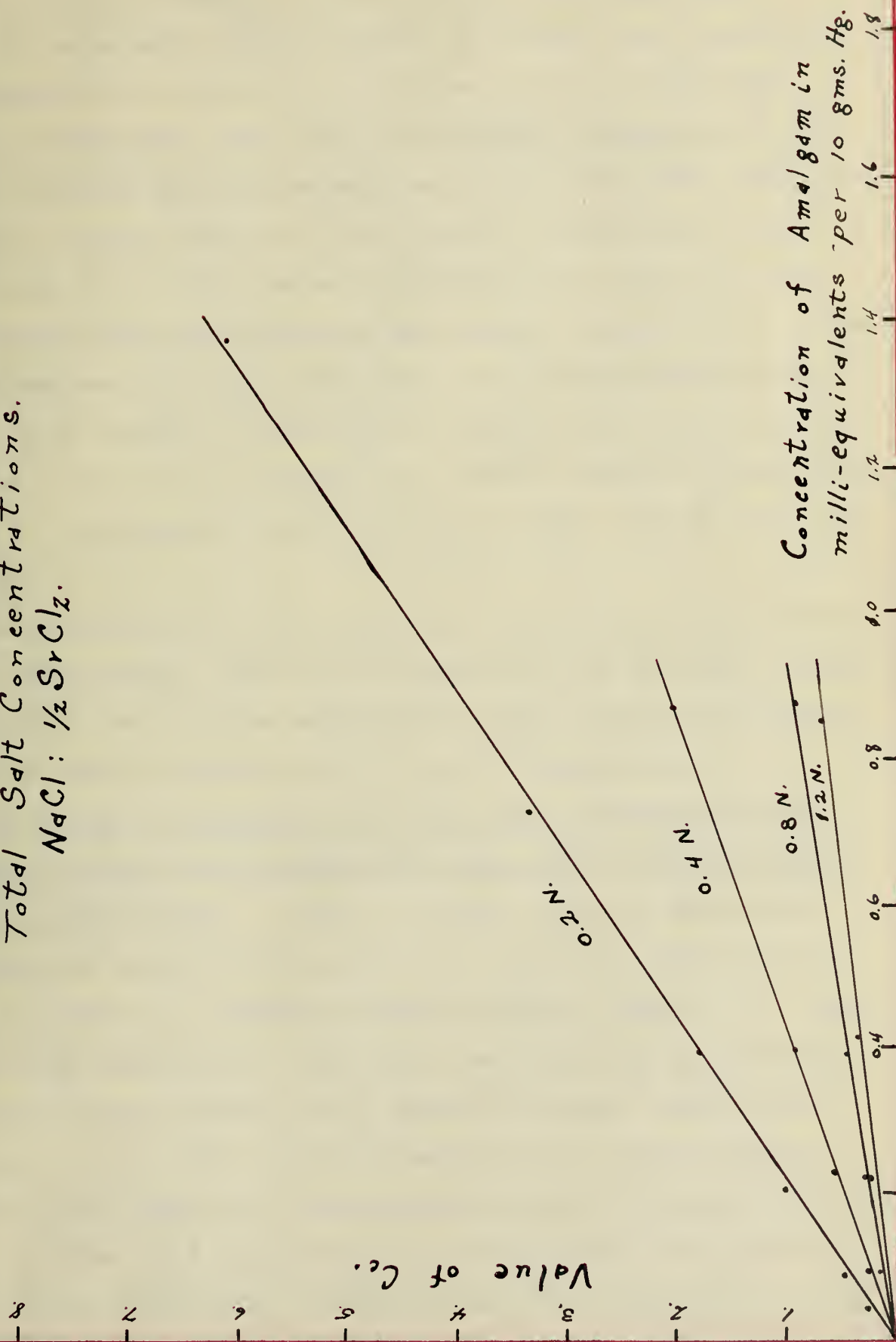
Temperature 25°

No.	Amal. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	C _c Cor. to A milli-equivs. per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na.	Sr.		
									<u>A = 0.753</u>
1.	Sr	.1765	.1740	48.7	0.899	.7241	.2759	.703	.589
2.	Sr	.1695	.1612	48.1	0.861	.7311	.2689	.675	.590
3.	Sr	.1735	.1700	47.3	0.908	.7252	.2748	.698	.579
4.	Na	.1706	.1545	50.3	0.812	.7413	.2587	.629	.583
5.	Na	.1710	.1505	50.3	0.805	.7462	.2538	.609	.570
6.	Na	.1696	.1560	49.5	<u>0.826</u>	.7378	.2622	.644	<u>.587</u>
				Mean	0.852			.660	.583
									<u>A = 0.390</u>
7.	Sr	.2190	.1155	100.0	0.434	.8306	.1694	.328	.295
8.	Sr	.2150	.1195	100.0	0.433	.8230	.1770	.349	.314
9.	Sr	.2165	.1140	100.7	0.426	.8308	.1692	.328	.300
10.	Na	.2012	.1075	100.3	0.399	.8290	.1710	.332	.325
11.	Na	.2035	.1040	100.7	0.397	.8352	.1648	.315	.310
12.	Na	.2056	.1021	100.4	<u>0.400</u>	.8389	.1611	.306	<u>.298</u>
				Mean	0.415			.326	.307
									<u>A = 0.225</u>
13.	Sr	.2420	.0825	199.4	0.216	.8842	.1158	.198	.206
14.	Sr	.2494	.0845	200.3	0.221	.8842	.1158	.198	.201
15.	Sr	.2488	.0837	198.7	0.223	.8848	.1152	.198	.199
16.	Na	.2440	.0823	200.2	0.216	.8847	.1153	.198	.206
17.	Na	.2540	.0819	200.7	0.223	.8891	.1109	.188	.190
18.	Na	.2500	.0825	200.5	<u>0.215</u>	.8892	.1108	.188	<u>.196</u>
				Mean	0.219			.195	.200
									<u>A = 0.0935</u>
19.	Sr	.2440	.0755	401.8	0.1060	.8932	.1068	.196	.173
20.	Sr	.2265*	.0597	398.3	(0.0962)	.9080	.0920	(.149)	(.145)
21.	Sr	.2400	.0665	402.0	0.1020	.9032	.0968	.159	.145
22.	Na	.2373	.0536	401.0	0.0978	.9221	.0779	.122	.117
23.	Na	.2320	.0435	400.5	0.0933	.9323	.0677	.104	.104
24.	Na	.2416	.0415	401.5	<u>0.0959</u>	.9376	.0624	<u>.0949</u>	<u>.0946</u>
				Mean	0.0990			.162	.127

* Sodium Sulphate spattered.

Curves showing value of C_c as a function
of Amalgam Concentration at different
Total Salt Concentrations.
 $\text{NaCl} : \frac{1}{2} \text{SrCl}_2$.

Fig. 2.



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variations in amalgam concentration of the above order, but with solutions of total normality of 0.4, 0.8 and 1.2 respectively. The results for experiments 19-24 of Table IV are far from concordant, but an explanation of this will be offered later (see page 38). While the results vary widely for the different concentrations of the salt solution, they are nevertheless for a given total salt concentration a linear function of the amalgam concentration, as is shown in Fig. 2, in which the mean (uncorrected) values of C_c are plotted against the mean values of the amalgam concentration. Since these values are all linear functions of the concentration of the amalgam, it of course follows that, at a given salt concentration the values of C_c can be corrected to a definite amalgam concentration by means of the proportion which obtains for that specific salt concentration.

The necessity for this correction arises from the fact that, owing to the variable evolution of hydrogen by the amalgam, the concentration of the latter at equilibrium is not constant, and hence the results would otherwise not be strictly comparable.

(2) Effect of increasing the total salt concentration at a fixed (equivalent) salt-concentration ratio, and at various fixed amalgam concentrations:- Table V contains the data obtained on increasing the total salt concentration, in stages, from 0.2 N to 3.2 N, the sodium and strontium chlorides being present in all cases in equivalent quantities. While the mean values of C_c , corrected to 0.225 milli-equivalents per 10 grams of mercury, vary all the way from 1.14 to 0.158, they nevertheless bear a rather definite relation to the total salt concentrations as may be seen by referring to Fig. 3; from 0.2 N up to about 1.2 N the values of C_c vary inversely as the total salt concentrations, and between these limits

Table V

Showing the effect of increasing the total salt concentration at a fixed (equivalent) salt-concentration ratio.

NaCl : 1/2 SrCl₂

Temperature 25°

No.	start	Amalg. Eq'm amalgam gave at on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	C _c Cor. to A milli-equivs. per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na.	Sr.		
Total Concentration 0.2 N.					(See Nos. 47-64 Table I) Mean				A = .225 .1.14
"					0.3 N.				
1.	Sr	.1699	.1675	200.4	0.210	.7240	.2760	.704	.749
2.	Sr	.1715	.1702	200.3	0.213	.7223	.2777	.711	.748
3.	Sr	.1737	.1697	201.1	0.213	.7229	.2771	.715	.750
4.	Na	.1666	.1621	195.5	0.210	.7266	.2734	.692	.737
5.	Na	.1703	.1656	200.0	0.210	.7266	.2734	.692	.738
6.	Na	.1714	.1647	200.3	<u>0.210</u>	.7291	.2709	<u>.681</u>	<u>.726</u>
Mean					0.211			.699	.741
Total Concentration 0.4 N.					(See Nos. 13-18 Table) Mean				.546
Total Concentration 0.6 N.									
7.	Sr	.2108	.1148	199.4	0.212	.8261	.1739	.341	.362
8.	Sr	.2147	.1180	201.2	0.216	.8262	.1738	.339	.354
9.	Sr	.2116	.1150	200.3	0.211	.8264	.1736	.340	.362
10.	Na	.2133	.1175	198.7	0.216	.8243	.1757	.346	.361
11.	Na	.2100	.1145	198.7	0.212	.8283	.1717	.334	.355
12.	Na	.2135	.1132	198.2	<u>0.213</u>	.8322	.1678	<u>.331</u>	<u>.350</u>
					0.213			.339	.357
Total Concentration 0.8 N.					(See Nos. 13-30 Table) Mean				.283
Total Concentration 1.2 N.					(See Nos. 13-18 Table) Mean				.200
Total Concentration 1.6 N.									
13.	Sr	.2935	.0958	197.2	0.263	.8871	.1129	.192	.164
14.	Sr	.2847	.0903	199.2	0.251	.8901	.1099	.185	.166
15.	Sr	.2847	.0944	199.3	0.253	.8856	.1144	.194	.172
16.	Na	.2548	.0739	200.2	0.229	.8986	.1014	.166	.171
17.	Na	.2618	.0759	200.3	0.225	.8986	.1014	.166	.166
18.	Na	.2528	.0720	199.7	<u>0.218</u>	.9001	.0999	<u>.165</u>	<u>.171</u>
					0.240			.178	.168
Total Concentration 2.4 N.									
19.	Sr	.2722	.0676	200.2	0.228	.9124	.0876	.141	.139
20.	Sr	.2571	.0815	200.5	0.225	.8910	.1090	.183	.183
21.	Sr	.2725	.0705	201.2	0.229	.9090	.0910	.147	.144
22.	Na	.2717	.0608	200.5	0.224	.9204	.0796	.126	.127
23.	Na	.2760	.0558	201.0	0.224	.9274	.0726	.142	.143
24.	Na	.2598	.0813	201.3	<u>0.222</u>	.9001	.0999	<u>.165</u>	<u>.167</u>
(Con't)					Mean	.224		.151	.150

No.	Amal. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	C _c Cor. to <u>A</u> milli-equivs, per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na.	Sr.		
Total Concentration 3.2 N.									<u>A</u> = .225
25.	Sr	.2902	.0985	198.7	0.259	.8841	.1159	.198	.161
26.	Sr	.2991	.0908	199.2	0.261	.8950	.1050	.175	.151
27.	Sr	.2970	.0930	198.5	0.262	.8924	.1076	.181	.155
28.	Na	.2656	.0826	201.4	0.227	.9005	.0995	.164	.163
29.	Na	.2575	.0879	201.0	(0.228)	.8835	.1165	(.199)	(.195) *
30.	Na	.2628	.0817	201.7	0.228	.8926	.1074	.180	.175
31.	Sr	.3260	.1100	206.0	0.281	.8986	.1014	.166	.133
32.	Sr	.3312	.1098	205.0	0.286	.8863	.1137	.193	.152
33.	Sr	.2908	.0961	199.5	0.258	.8868	.1132	.192	.167
34.	Na	.2480	.0880	200.1	(0.222)	.8794	.1206	(.208)	(.211) *
35.	Na	.2505	.0841	200.0	(0.225)	.8868	.1132	(.192)	(.192) *
36.	Na	.2650	.0836	200.2	<u>0.228</u>	.8992	.1008	<u>.167</u>	<u>.164</u>
					0.254			.179	.158

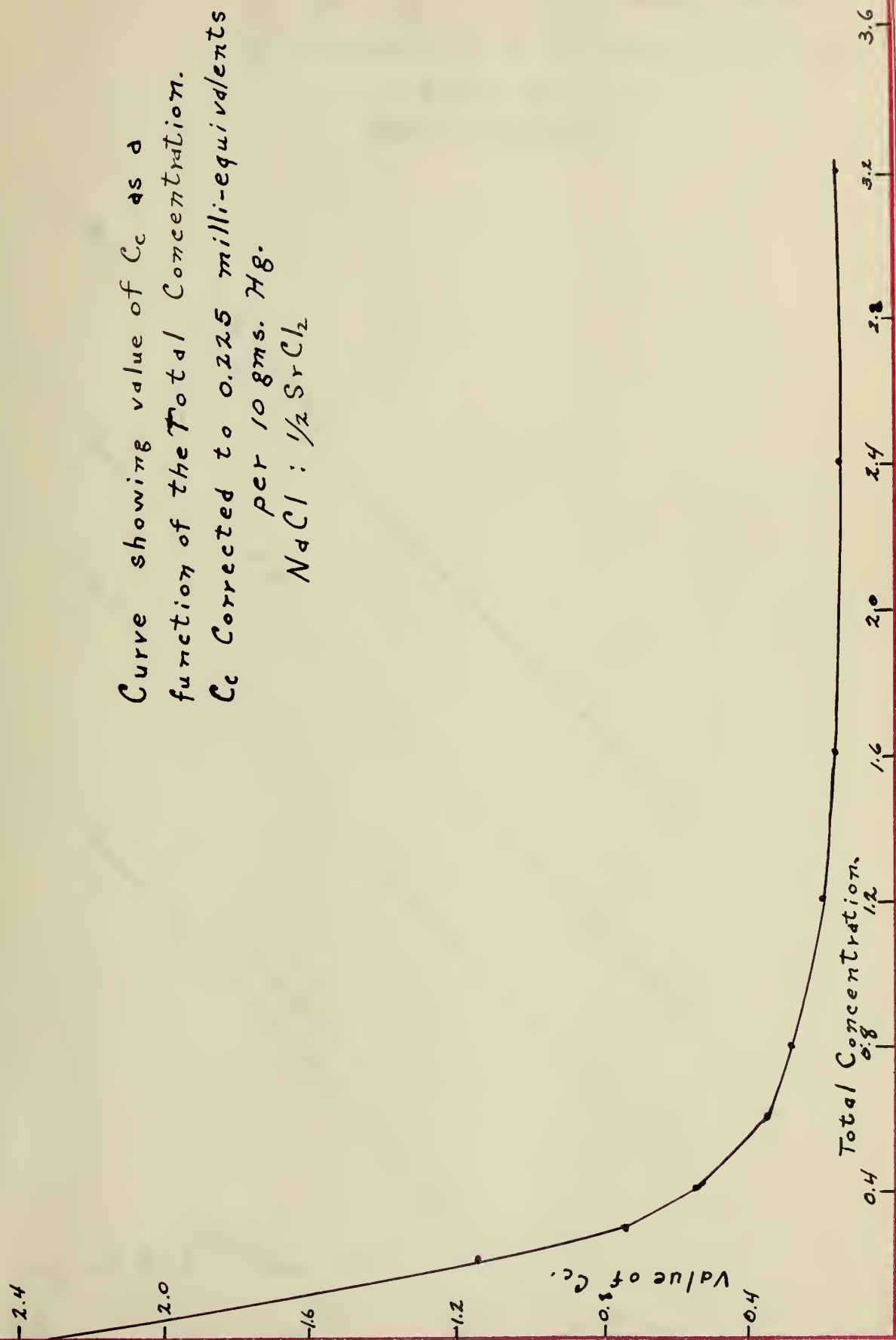
* Hydrogen evolved quite freely.

the curve is a hyperbola. If, therefore, instead of plotting the values of C_c and of the total concentration, the logarithmic values are plotted, the logarithm of C_c is approximately a linear function of the logarithm of the the total concentration; this is shown by curve (3) of Fig. 4.

With the exception of experiments 19-24 the results are very concordant, i.e., the extremes differ in each set by not over 4 or 5%, this being the limit of accuracy with which the values of C_c could be checked. However, this variation (due to analytical error) is small in comparison with the large variation due to differences in concentration in the amalgams and solutions.

The values in Table V were all calculated for a single specific concentration of amalgam; but data suitable for studying the effect of increasing the salt concentrations at other fixed amalgam concentrations are to be found in the preceding tables, and for this purpose the mean values in all cases are again tabulated in Table VI.

Curve showing value of C_c as a
function of the Total Concentration.
 C_c Corrected to 0.225 milli-equivalents
per 10 gms. Hg.
 $\text{NaCl} : \frac{1}{2} \text{SrCl}_2$



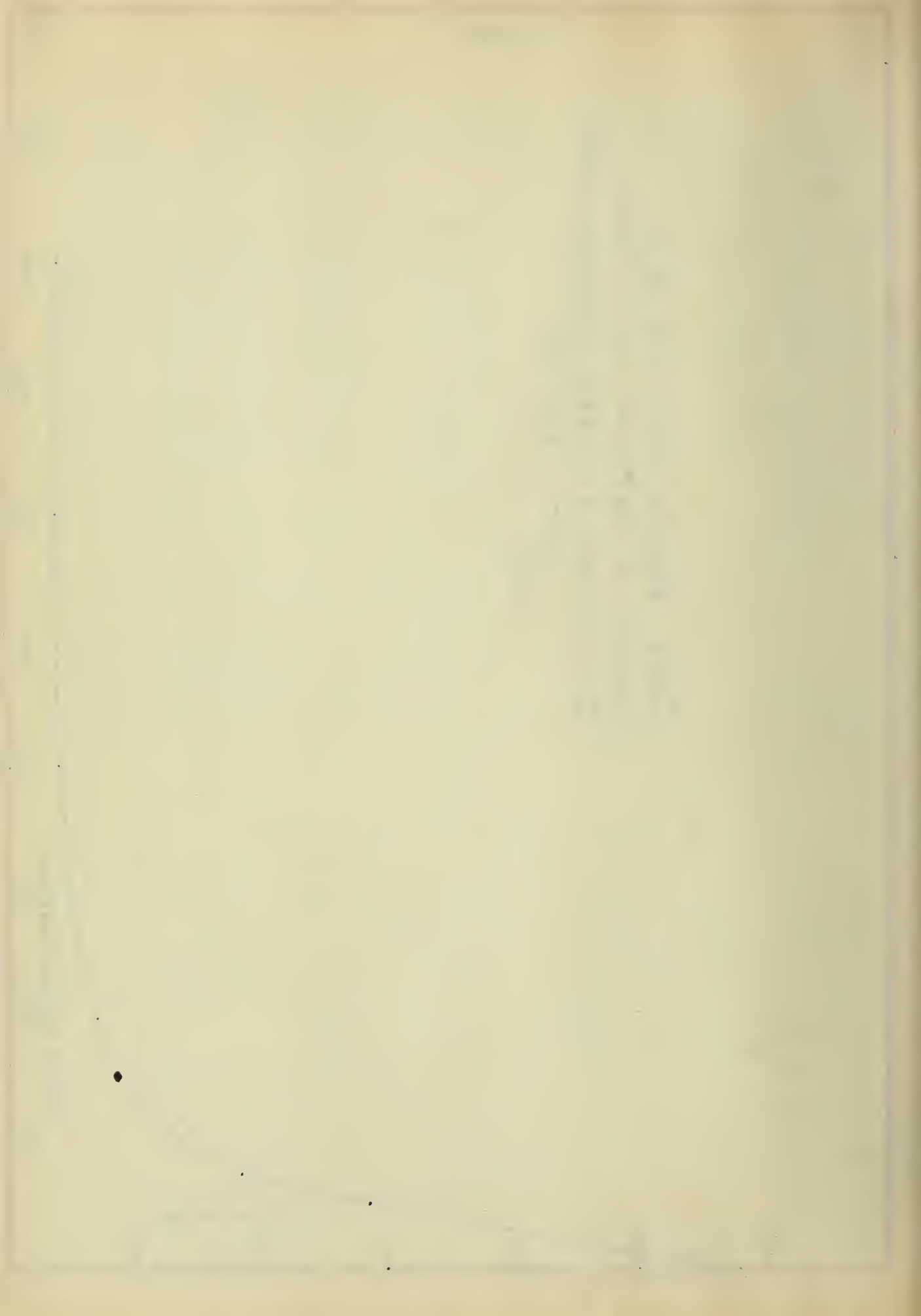


Fig. 4.

Curves showing $\text{Log. of } C_c$ as a function
of the $\text{Log. of Total}^{\text{salt}} \Delta \text{Concentration.}$

C_c Corrected to A milli-equivalents per
10 gms. Hg.

$\text{NaCl} : \frac{1}{2} \text{SrCl}_2$

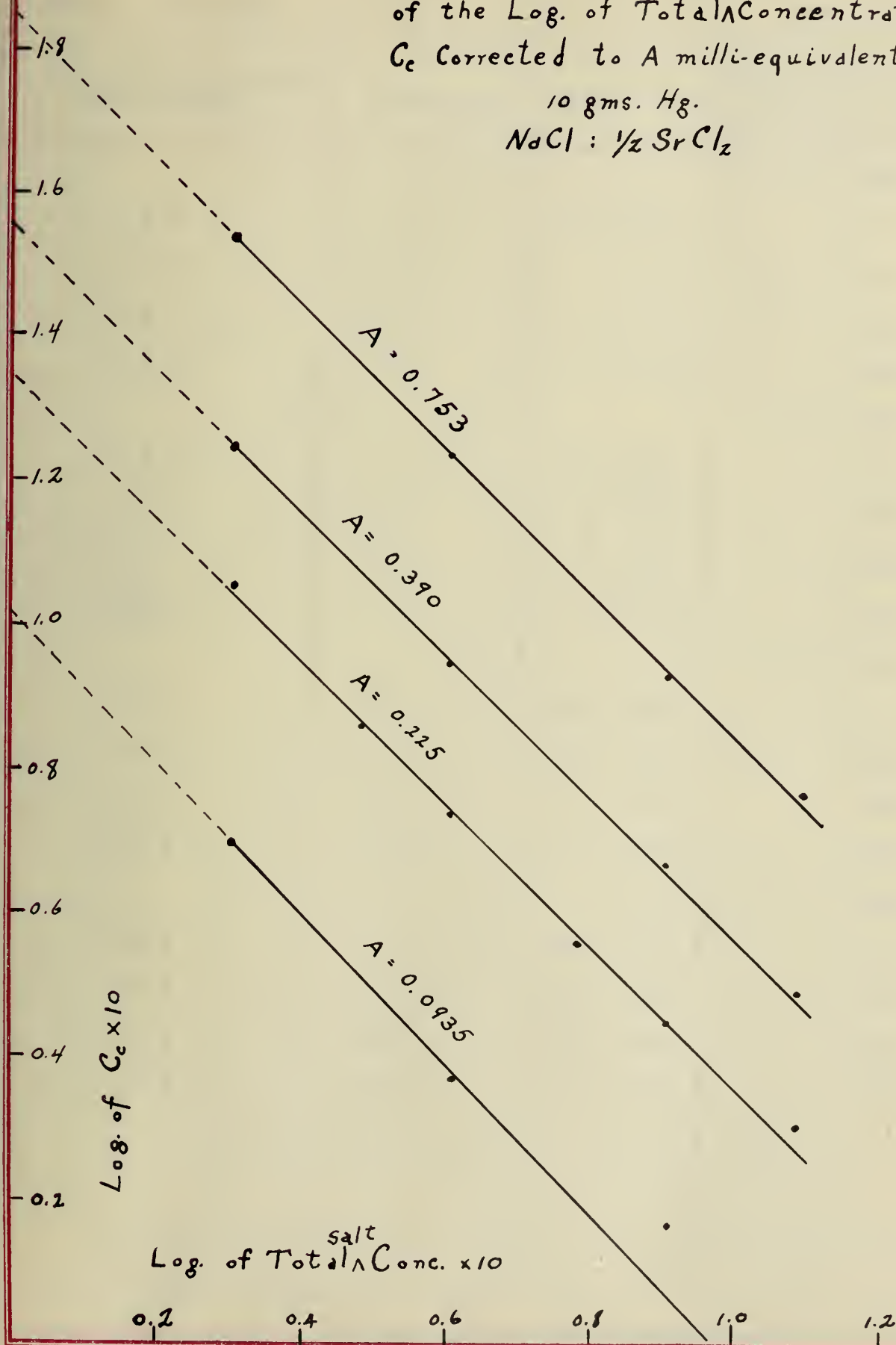


Table VI

NaCl : 1/2 SrCl₂

Temperature 25°

Total Concentration of Solution.	Table No.	Exps. Nos.	Mean values of C_c corrected to \underline{A} milli-equivalents per 10 grams mercury
			$\underline{A} = 0.753$
0.2 N	I	23 - 34	3.51
0.4 N	II	1 - 6	1.72
0.8 N	III	1 - 6	.843
1.2 N	IV	1 - 6	.593
			$\underline{A} = 0.390$
0.2 N	I	35 - 46	1.76
0.4 N	II	7 - 12	.896
0.8 N	III	7 - 12	.462
1.2 N	IV	7 - 12	.307
			$\underline{A} = 0.225$
0.2 N	I	47 - 64	1.14
0.4 N	II	13 - 18	.546
0.8 N	III	13 - 30	.283
1.2 N	IV	13 - 18	.200
			$\underline{A} = 0.0935$
0.2 N	I	65 - 70	.490
0.4 N	II	19 - 24	.251
0.8 N	III	31 - 36	.151
1.2 N	IV	19 - 24	.127

In this table column one gives the total concentration of the solution; column two the number of the table in which the individual experiments are tabulated; column three refers numerically to the experiments, and column four contains the mean corrected values of C_0 .

The logarithms of these mean values plotted against the logarithms of the total salt concentrations are also shown in Fig. 4.

These curves which are practically parallel show very conclusively that the effect due to increasing the total salt concentration of the solution is entirely independent of the effect due to varying the concentration of the amalgam. This will be shown in detail under the discussion of the ion-fractions.

(3) Effect of varying the concentration ratio of the salts at a fixed total concentration:- Tables VII and VIII give the data obtained at total concentrations of 0.3 N and 0.6 N, respectively, upon varying the ratio of the salts from $1/2 \text{ SrCl}_2 : \text{NaCl} = 4 : 1$ to $1/2 \text{ SrCl}_2 : \text{NaCl} = 1 : 4$. The mean values do not follow any regular order of change as will be seen upon referring to Fig. 5, in which the values of C_0 are plotted against the mol-fractions of the salts in the solution.

It should be noted that the normality ratios for experiments 1-6 of Table VII are 0.071 NaCl to 0.229 SrCl_2 instead of 0.06 and 0.24 as was intended. Since the mean values are not regular this discrepancy was not detected until the ion-fractions were calculated when it was found they did not agree. Upon analysis of some of the remaining solution the NaCl was found to be 0.0700 and 0.0711 N and the SrCl_2 to be 0.2289 and 0.2290 N. Therefore these values were used.

The first six experiments in Table VII also show a greater variation than usual in the different values of C_0 , the range being

Table VII

Total Concentration 0.3 N.

Temperature 25°.

No.	Amalg. start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	C _c Cor. to \bar{A} milli-equivs. per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na	Sr		
NaCl = 0.071 N, SrCl ₂ = 0.229 N,									$\bar{A} = .225$
1.	Sr	.0860	.2760	200.8	0.210	.4462	.5538	.668	.716
2.	Sr	.0885	.2973	202.4	0.220	.4293	.5707	.744	.760
3.	Sr	.0855	.2806	201.0	0.212	.4407	.5593	.692	.734
4.	Na	.0824	.2634	200.5	0.201.	.4471	.5529	.664	.744
5.	Na	.0840	.2613	200.4	0.201	.4539	.5461	.637	.713
6.	Na	.0818	.2475	200.4	<u>0.192</u>	.4608	.5392	.610	<u>.715</u>
Mean					0.206			.669	.730
NaCl = 0.10 N, SrCl ₂ = 0.20 N.									
7.	Sr	.1195	.2535	200.1	0.210	.5705	.4295	.660	.706
8.	Sr	.1147	.2212	197.5	0.204	.5729	.4271	.651	.719
9.	Sr	.1164	.2288	200.0	0.207	.5681	.4319	.669	.729
10.	Na	.1127	.2117	200.0	0.195	.5792	.4208	.627	.725
11.	Na	.1145	.2129	200.0	0.197	.5819	.4181	.617	.708
12.	Na	.1130	.2147	200.8	<u>0.196</u>	.5764	.4236	<u>.638</u>	<u>.733</u>
Mean					0.202			.644	.720
NaCl = 0.15 N, SrCl ₂ = 0.15 N. (See Nos. 1-6 Table) Mean									.741
NaCl = 0.20 N, SrCl ₂ = 0.10 N.									
13.	Sr	.2235	.0935	199.4	0.209	.8608	.1392	.601	.649
14.	Sr	.2117	.0853	199.8	0.196	.8653	.1347	.576	.662
15.	Sr	.2200	.0923	200.3	0.205	.8605	.1395	.603	.662
16.	Na	.2028	.0802	200.5	0.186	.8737	.1263	.530	.640
17.	Na	.2097	.0838	200.3	0.193.	.8662	.1338	.571	.668
18.	Na	.2127	.0842	199.3	<u>0.196</u>	.8674	.1326	<u>.564</u>	<u>.646</u>
Mean					0.198			.574	.654
NaCl = 0.24 N, SrCl ₂ = 0.06 N.									
19.	Sr	.2580	.0585	200.6	0.213	.9208	.0792	.664	.706
20.	Sr	.2507	.0530	199.8	0.206	.9231	.0769	.642	.701
21.	Sr	.2560	.0560	200.3	0.210	.9220	.0780	.652	.698
22.	Na	.2523	.0523	200.0	0.206	.9253	.0747	.620	.679
23.	Na	.2495	.0515	200.0	0.204	.9262	.0738	.612	.677
24.	Na	.2500	.0510	200.5	<u>0.203</u>	.9270	.0730	<u>.604</u>	<u>.669</u>
Mean					0.207			.632	.688

Table VIII

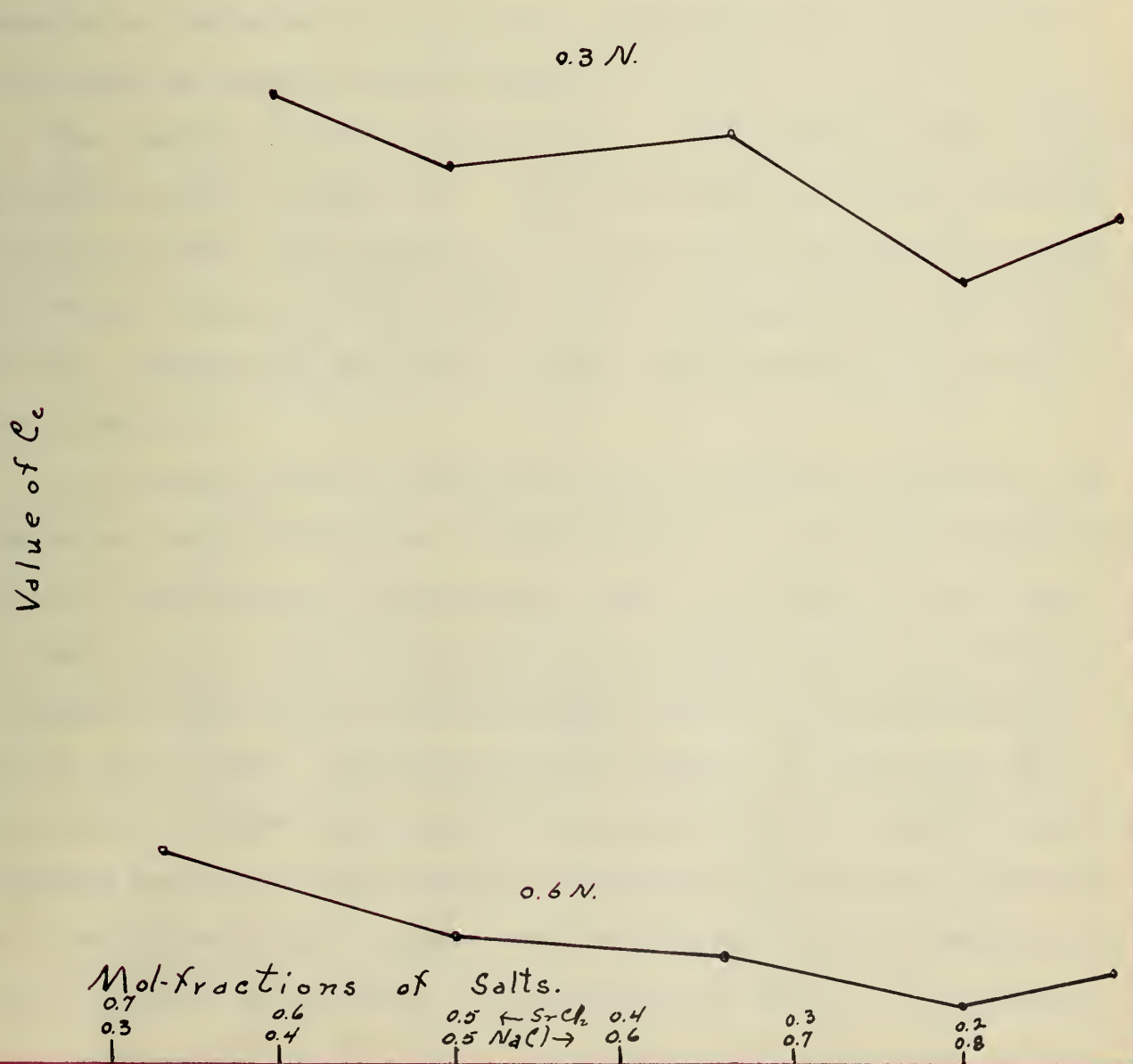
Showing the effect of varying the concentration ratio of the salts at a fixed total concentration.

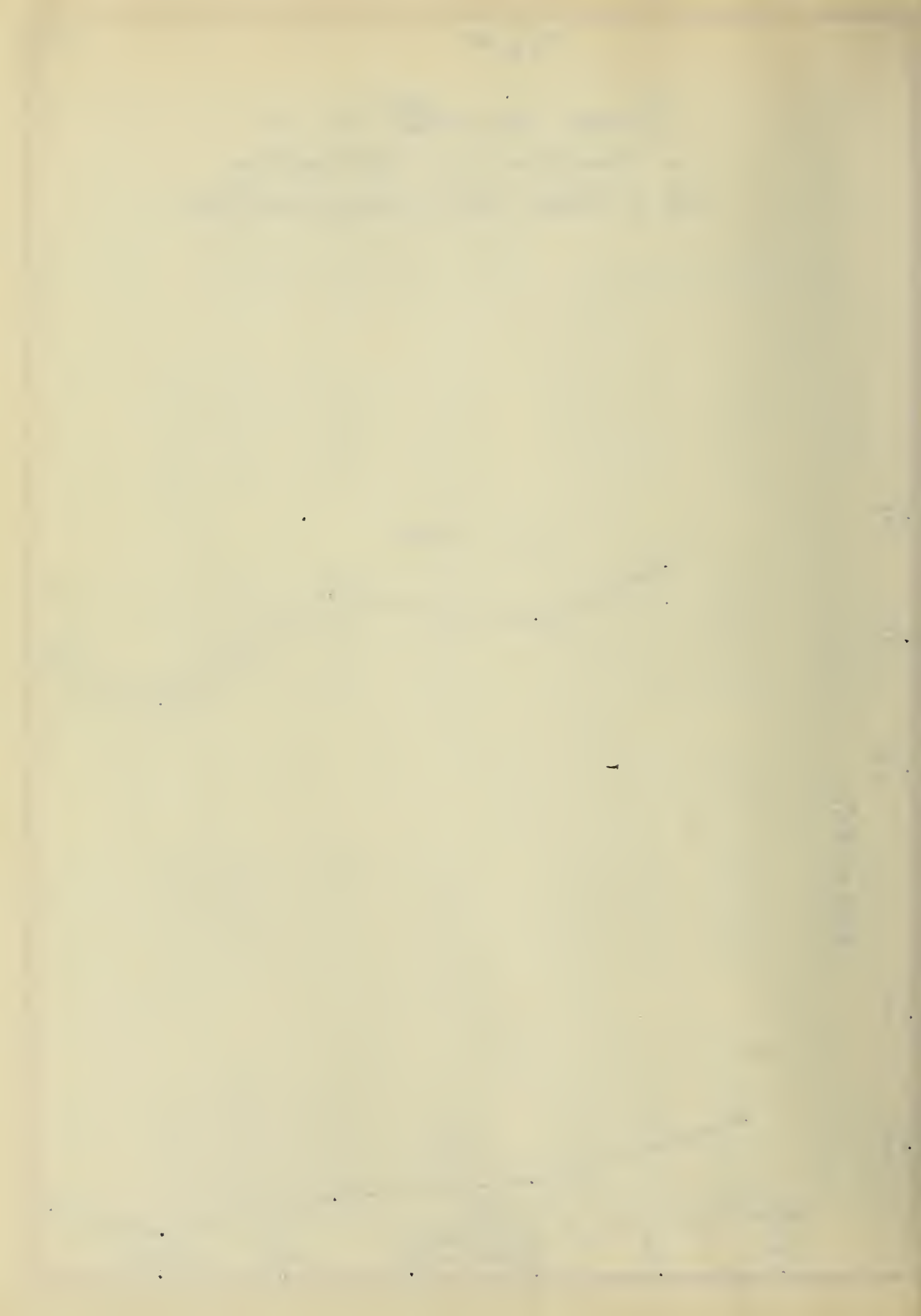
Total Concentration 0.6 N.

Temperature 25°.

No.	Amalg. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic fractions of amalgamated metals		C _c	C _c Cor. To A milli-equivs. per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na.	Sr.		
	NaCl	= 0.12 N, SrCl ₂ = 0.48 N.							A = .225
1.	Sr	.0815	.2190	193.5	0.183	.4906	.5094	.353	.435
2.	Sr	.0845	.2318	194.5	0.191	.4894	.5106	.355	.419
3.	Sr	.0910	.2470	199.5	0.199	.4878	.5122	.358	.406
4.	Na	.0833	.2125	191.5	0.182	.5034	.4966	.326	.404
5.	Na	.0835	.2195	201.5	0.177	.4960	.5040	.341	.435
6.	Na	.0813	.2125	200.0	<u>0.173</u>	.4978	.5022	<u>.337</u>	<u>.445</u>
				Mean	0.184			.345	.424
	NaCl	= 0.20 N, SrCl ₂ = 0.40 N.							
7.	Sr	.1450	.1639	200.0	0.191	.6959	.3041	.314	.369
8.	Sr	.1494	.1665	200.2	0.196	.6990	.3010	.314	.362
9.	Sr	.1470	.1715	195.2	0.202	.6891	.3109	.327	.365
10.	Na	.1354	.1427	200.7	0.172	.7105	.2895	.287	.374
11.	Na	.1335	.1435	195.5	0.176	.7065	.2935	.294	.376
12.	Na	.1396	.1555	200.0	<u>0.183</u>	.6985	.3015	<u>.309</u>	<u>.380</u>
				Mean	0.170			.307	.371
	NaCl	= 0.30 N, SrCl ₂ = 0.30 N. (See Nos. 7-12 Table)							Mean .357
	NaCl	= 0.40 N, SrCl ₂ = 0.20 N.							
13.	Sr	.2565	.0588	199.8	0.213	.9186	.0814	.309	.327
14.	Sr	.2585	.0613	200.0	0.216	.9160	.0840	.319	.333
15.	Sr	.2620	.0615	199.8	0.218	.9175	.0825	.314	.324
16.	Na	.2348	.0500	200.0	0.193	.9240	.0760	.285	.333
17.	Na	.2467	.0545	198.4	0.204	.9209	.0791	.298	.330
18.	Na	.2457	.0553	201.2	<u>0.202</u>	.9200	.0800	<u>.303</u>	<u>.337</u>
				Mean	0.208			.305	.331
	NaCl	= 0.48 N, SrCl ₂ = 0.12 N.							
19.	Sr	.2300	.0230	191.0	0.183	.9622	.0378	.291	.357
20.	Sr	.2730	.0300	200.0	0.209	.9593	.0407	.314	.339
21.	Sr	.2717	.0305	199.6	0.208	.9584	.0416	.322	.349
22.	Na	.2691	.0301	200.3	0.206	.9573	.0427	.331	.362
23.	Na	.2674	.0305	200.0	0.205	.9578	.0422	.327	.367
24.	Na	.2606	.0278	200.3	<u>0.198</u>	.9605	.0395	<u>.304</u>	<u>.343</u>
				Mean	0.201			.315	.353

Curves showing ^{value} λ of C_e as
a function the Mol-fraction
at a fixed Total Concentration.

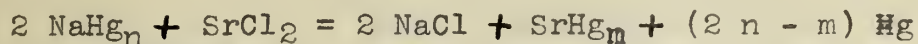




from .713 to .760 or a difference of about 7 %.

(4) Effect of changing the temperature: Heat of reaction:- The

The heat of the reaction



may be determined from the values of C_c at different temperatures, other conditions remaining constant, by the Van't Hoff equation

$$2.303 \log \frac{C_{c1}}{C_{c2}} = \frac{Q}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

in which C_{c1} and C_{c2} are the equilibrium values at the temperatures T_1 and T_2 respectively, R the gas constant in calories or 1.986 and Q the heat evolved when the substances in the numerator react to form those in the denominator of the mass law expression, or when the above reaction takes place from right to left.

The results for the values of C_c as determined at 15° , 20° , 25° and 30° are given in Table IX. By substituting the mean values of C_c into the Van't Hoff equation, the heat of the reaction was found to be 2987 Cal. between 15° and 20° ; 4665 Cal. between 20° and 25° ; and 4430 Cal. between 25° and 30° ; the mean value between 15° and 30° being 4024 Cal.

The results are of course far from concordant, but when it is considered that a difference of approximately 1 % in the determination of the C_c value makes a difference of 400 to 500 Cal. in the heat of the reaction, and that the individual determinations of C_c could not be checked within narrower limits than 4 or 5 %, the agreement is perhaps not so bad. Nevertheless the heat of the reaction, as determined, includes the heat of dissociation of the metallic mercury compounds as well as the heat of ionization of the salts, and these may (and probably do) change very materially with the temperature. Since the "Heat of reaction" as determined is really the algebraic

Table IX

the
Showing effect of changing the temperature.

Total Concentration 0.2 N.

NaCl : 1/2 SrCl₂

No.	Amalg. at start	Eq'm amalgam gave on analysis.			Amalg. Conc. in milli-equivs. per 10 gms. Hg.	Atomic frac-tions of amal-gamated metals		C _c	Cor.tp A milli-equivs. per 10 gms. Hg.
		Na ₂ SO ₄	SrSO ₄	Hg.		Na	Sr		
Temperature 15°									A = .225
1.	Sr	.1442	.1587	189.2	0.199	.7015	.2985	.811	.919
2.	Sr	.1511	.1700	195.0	0.204	.6968	.3032	.835	.920
3.	Sr	.1465	.1590	198.0	0.192	.7043	.2957	.797	.935
4.	Na	.1395	.1405	189.0	0.184	.7179	.2821	.749	.915
5.	Na	.1430	.1428	194.5	0.184	.7215	.2785	.715	.877
6.	Na	.1121	.0985	179.4	0.148	.7466	.2534	.610	.919
Mean					0.185			.753	.912
Temperature 20°.									
7.	Sr	.1431	.1675	190.0	0.201	.6877	.3123	.882	.988
8.	Sr	.1355	.1659	189.5	0.196	.6788	.3212	.931	1.07
9.	Sr	.1340	.1510	191.5	0.184	.6965	.3035	.836	1.02
10.	Na	.1361	.1495	191.5	0.185	.7019	.2981	.821	.998
11.	Na	.1500	.1735	200.5	0.200	.6909	.3091	.865	.975
12.	Na	.1455	.1622	201.0	0.190	.6992	.3008	.841	.997
13.	Sr	.1570	.1902	195.5	0.219	.6809	.3191	.920	.945
14.	Sr	.1588	.2007	200.3	0.221	.6717	.3283	.972	.991
15.	Sr	.1602	.2023	202.0	0.221	.6717	.3283	.972	.991
16.	Na	.1461	.1613	200.4	0.191	.7008	.2992	.812	.962
17.	Na	.1445	.1602	199.5	0.189	.7000	.3000	.820	.979
18.	Na	.1401	.1646	200.0	0.188	.6877	.3123	.882	1.05
Mean					0.199			.879	.997
Temperature 25° (See Nos. 47-64 Table I)									Mean 1.14
Temperature 30°.									
19.	Sr	.1095	.1320	194.0	0.154	.6820	.3180	.913	1.34
20.	Sr	.1131	.1334	200.5	0.152	.6869	.3131	.887	1.31
21.	Sr	.1205	.1450	198.8	0.168	.6832	.3168	.907	1.24
22.	Na	.1115	.1208	200.3	0.148	.6921	.3079	.859	1.31
23.	Na	.1116	.1273	200.5	0.148	.6941	.3069	.851	1.30
24.	Na	.1185	.1423	201.0	0.161	.6828	.3172	.907	1.25
Mean					0.155			.887	1.29

sum of the heats of several (at least five) individual reactions, the values obtained are of significance mainly with respect to the order of magnitude and the direction. Since the heat of the reaction is positive the reaction as a whole is exothermic.

(5) Calculation of the ion-fractions in cases (2) and (3):-

In the theoretical part an expression $(Na) = \frac{-1 + \sqrt{1 + 4a}}{2a}$ has been developed, in which " a " = $\frac{C_c (SrCl_2)}{C_o (NaCl)^2}$. From the data now at hand it is possible to calculate the change of ion-fraction (a) with the change of total concentration of the solution at a fixed salt-concentration ratio, and (b) with the change of concentration ratio at a fixed total salt concentration.

(a) By the extrapolation of the logarithmic curve (No.3, Fig 4) a C_o value of 2.32 is obtained at an amalgam concentration of 0.225 milliequivalents per 10 grams of mercury. By using this value and the necessary data from Table V the ion-fractions have been calculated over a total concentration range of 0.2 N to 3.2 N, and are given in Table X. Column one gives the total normality of the solution; column two the value of C_o ; column three the values of C_c from Table V; and columns five and six the calculated ion-fractions.

Table X

NaCl : 1/2 SrCl₂

Temperature 25°

Amalgam = 0.225 milli-equivalents per 10 grams mercury.

Total Normality	C_o	C_c	Calculated ion-fractions	
			Na	Sr
0.00	2.32	2.32	.666	.333
0.20	2.32	1.14	.777	.223
0.30	2.32	.741	.835	.165
0.40	2.32	.546	.866	.134
0.60	2.32	.357	.900	.100
0.80	2.32	.283	.920	.080
1.20	2.32	.200	.943	.057
1.60	2.32	.168	.951	.049
2.40	2.32	.150	.955	.045
3.20	2.32	.158	.955	.045

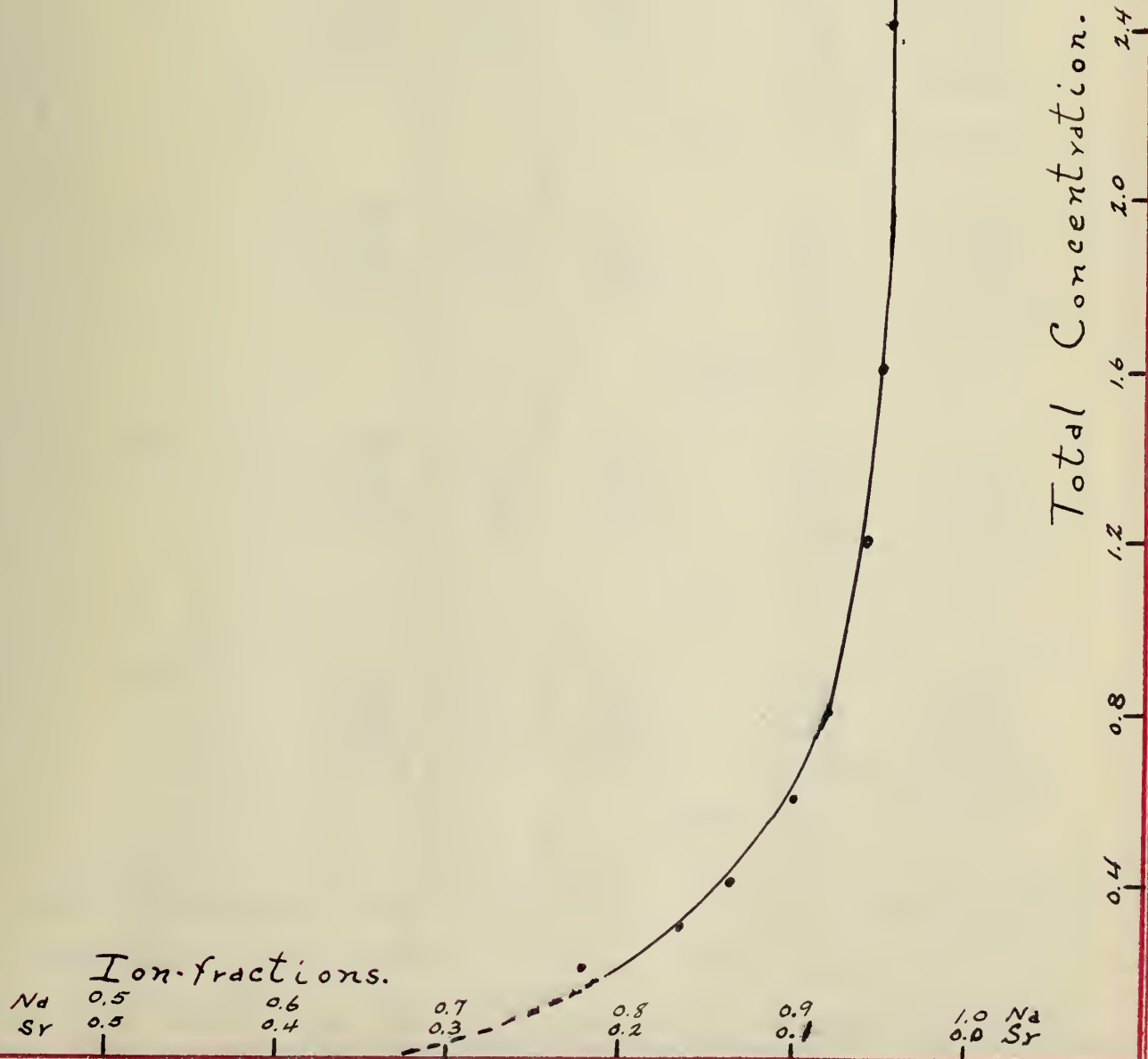
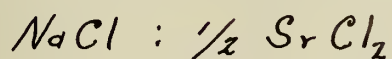
From these data it may be readily noted that the sodium ion-fraction increases from 0.777 at a total concentration of 0.2 N to 0.951 at 1.6 N, and that above this concentration it is practically constant; the strontium ion-fraction decreases correspondingly. The rate of this change may be seen more plainly by referring to Fig. 6, in which the ion-fractions are plotted against the total salt concentration. The curve is extrapolated to an ion-fraction of 0.666 sodium to 0.333 strontium, the theoretical values at infinite dilution when the salts have equal normality in the solution.

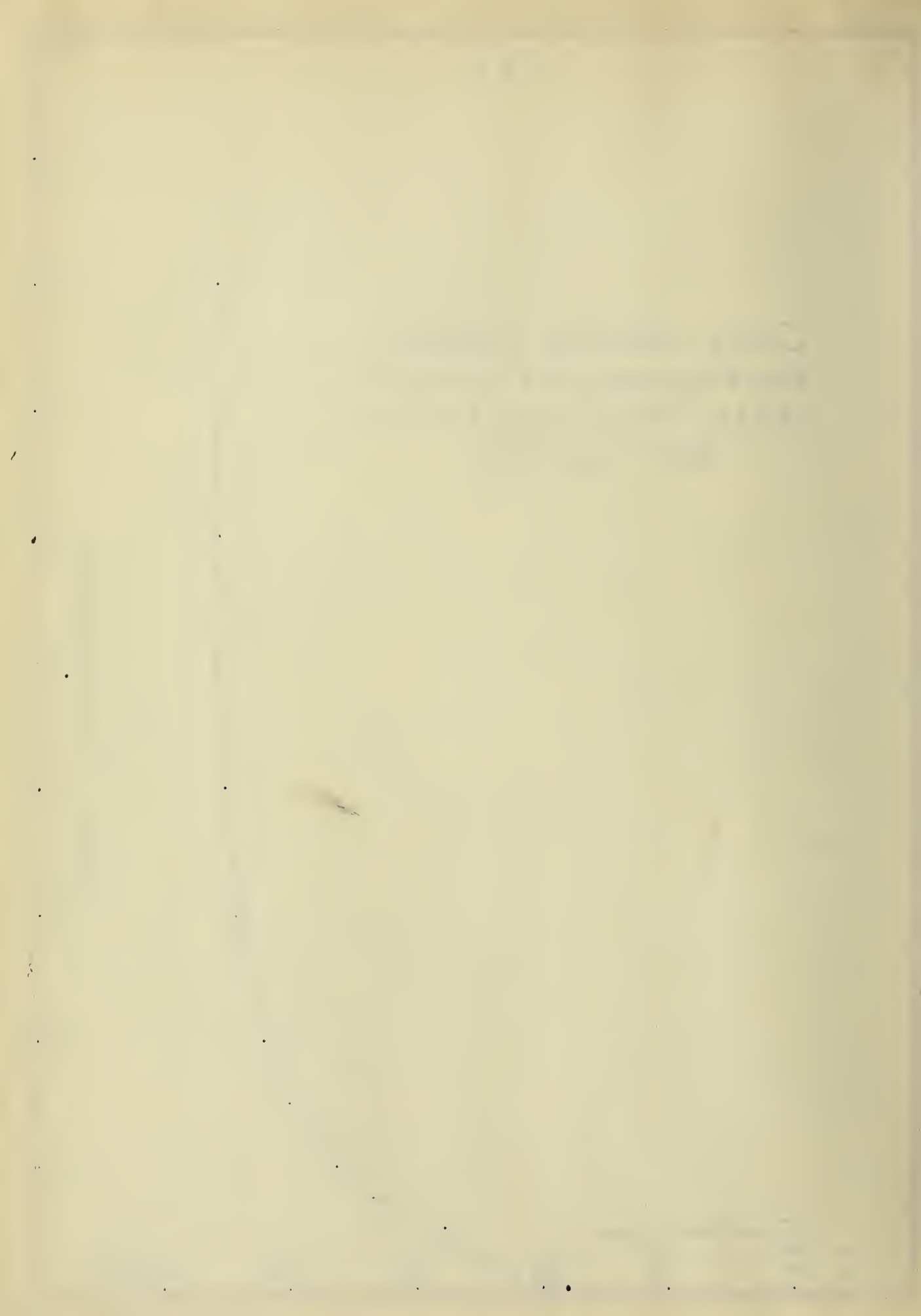
From the previous data it has been shown that the value of C_0 changes with the concentration of the amalgam. On plotting the logarithmic values of C_0 against the logarithm of the total concentration for four different specific amalgam concentrations, a series of four parallel curves was obtained, and the statement was made (page 28) that the change of C_0 caused by varying the concentration of the amalgam is independent of the change caused by the increase of total salt concentration at a fixed (equivalent) concentration ratio. If this is true the ion-fraction values calculated from the four sets of data should be identical. Also if the principle, namely, the mass law, upon which this investigation is based, is true then the ion-fractions calculated in all four cases for a given concentration of solution should agree; the constitution of a solution of any specific salt ratio and concentration must of necessity remain constant regardless of the composition of the amalgam with which it is in equilibrium.

On extrapolating curves 1, 2, and 4, in Fig. 6, C_0 values are obtained as follows; when "A" = 0.753, C_0 = 6.92; when "A" = 0.390, C_0 = 3.51; and when "A" = 0.0935, C_0 = 1.07, where "A" stands for milli-equivalents of amalgamated metals per 10 grams of mercury.

Fig. 6.

Curve showing calculated
Ion-fractions as a function
of the Total Concentration.





For purposes of comparison, the ion-fractions as calculated from the data in Table VI at the total concentrations of 0.2, 0.4, 0.8 and 1.2 N and for the amalgam concentrations given above are tabulated in Table XI; in which column one gives the number of the calculation; column two the total normality of the solution, column three the value of "A", columns four and five the respective C_o and C_c values, and columns six and seven the calculated ion-fractions.

Table XI

No.	Total Normality	"A"	C_o	C_c	Calculated ion-fractions	
					Na	Sr
1.	0.2	0.753	6.92	3.51	.776	.223
2.		0.390	3.51	1.76	.750	.250
3.		0.225	2.32	1.14	.777	.223
4.		0.0935	1.07	.490	<u>.786</u>	<u>.214</u>
					Mean .772	.228
5.	0.4	0.753	6.92	1.72	.861	.139
6.		0.390	3.51	.896	.860	.140
7.		0.225	2.32	.546	.866	.134
8.		0.0935	1.07	.251	<u>.873</u>	<u>.127</u>
					Mean .865	.135
9.	0.8	0.753	6.92	.843	.922	.078
10.		0.390	3.51	.462	.898	.102
11.		0.225	2.32	.283	.920	.080
12.		0.0935	1.07	.151	<u>.913</u>	<u>.087</u>
					Mean .913	.087
13.	1.2	0.753	6.92	.583	.942	.058
14.		0.390	3.51	.307	.941	.059
15.		0.225	2.32	.200	.943	.057
16.		0.0935	1.07	(.127)	<u>(.914)</u>	<u>(.086)</u>
					Mean .942	.058

The ion-fraction values are in the case of each salt solution very concordant for the different amalgam concentrations, with the exception of those in No, 16; the C_c value upon which these values are

based is not reliable, it being the mean value of experiments 19-24 in Table IV. Attention has already been called to the variation of these values; at this very high total salt concentration the ion-fraction of the strontium in the solution is exceedingly low, and since the very low concentration (i.e. large volume) of the amalgam decreases the active mass of the strontium in the amalgam, (see page 41) it is easily seen especially upon referring to the original data in Table IV, that equilibrium probably was not attained in the case of these experiments.

The concordance of these values may then be taken as further evidence that, in so far as the ions are concerned, the mass law does hold for concentrated solutions of strong electrolytes, and that the principles upon which this investigation is based are true.

(b) The change of ion-fraction with the change of mol-fraction at a fixed total salt concentration may be determined from the data in Tables VII and VIII. As these determinations were performed at a total amalgam concentration of 0.225 milli-equivalents per 10 grams of mercury, the previously determined value of C_0 at this amalgam concentration, 2.32, is the value used here. The results of these calculations at 0.3 and 0.6 N are given in Table XII, in which columns one and two represent the mol-fractions of the NaCl and the SrCl_2 in the solution, column three the C_0 value, and columns four and five the calculated ion-fractions of Na^+ and Sr^{++} respectively.

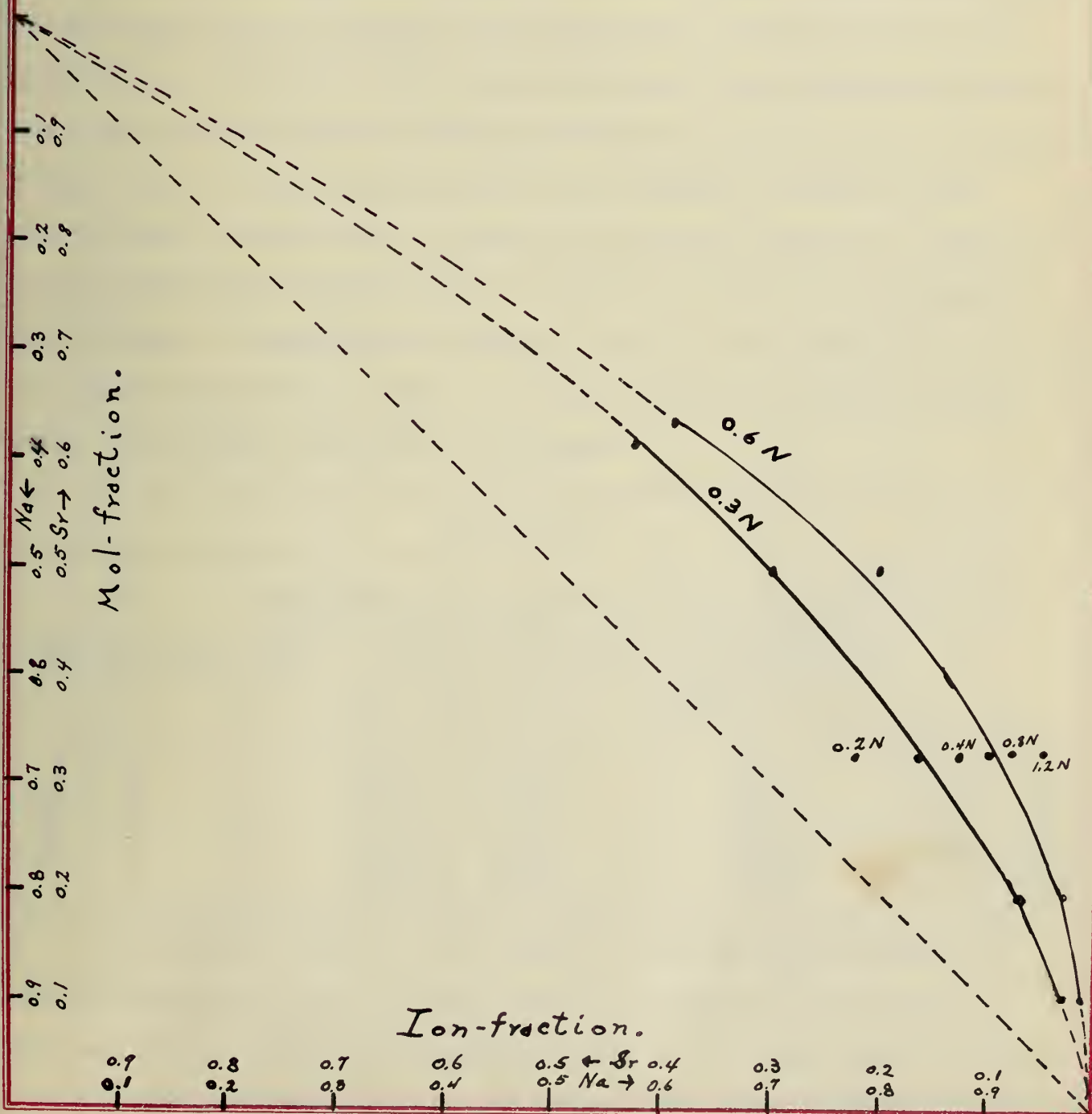
By reference to Fig. 7, in which ^{the} mol-fractions of the salts in the solutions are plotted against the corresponding ion-fractions, it is evident that the ion-fractions are by no means proportional to the mol-fractions of the salts. If they were proportional these ratios would be identical and the curve would be a straight

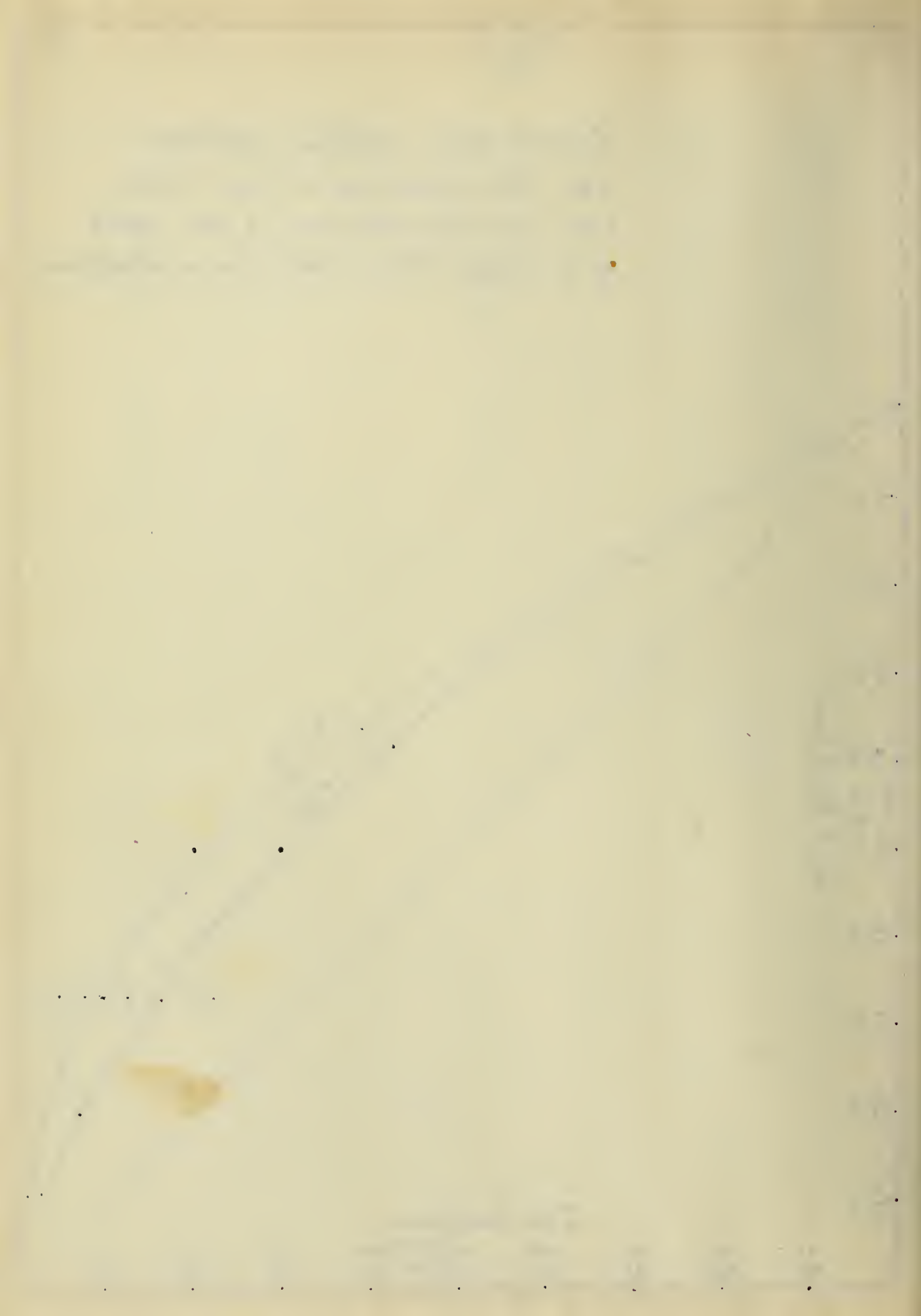
Table XII

Mol-fractions of the salts in the solution.		C_c	Calculated ion-fractions.	
NaCl	SrCl ₂		Na	Sr
Total concentration 0.3 N.				
.3845	.6155	.730	.567	.431
.5000	.5000	.720	.697	.303
.6666	.3333	.741	.835	.165
.8000	.2000	.654	.926	.074
.8888	.1111	.688	.966	.034
Total Concentration 0.6 N.				
.3333	.6666	.424	.602	.398
.5000	.5000	.370	.797	.203
.6666	.3333	.357	.900	.100
.8000	.2000	.331	.969	.031
.8888	.1111	.353	.980	.020

line cutting the plot diagonally as shown by the broken line. The fact that the ion-fractions are not proportional to the mol-fractions in the solution is the point that is used to prove that the mass law does not hold for concentrated solutions. In this paper, an application of the law itself shows that the ion-fractions are not proportional to the mol-fractions in the solutions; that is, the use of the mass law leads to the very conclusion that has been used against it, so that it may after all hold for concentrated solutions. If the mass law does hold in such solutions then it follows that in the case of mol-fractional variations at other total salt concentrations, a series of curves should exist which would approach the theoretical straight line as their limit at zero concentration. The two curves already given, showing the change of ion-fraction at total concentrations of 0.6 N and 0.3 N respectively, seem to point to the correctness of this conclusion. Moreover, on plotting in Fig. 7 the mean values of the ion-fractions found to be present in equivalent mixtures at total concentrations of 0.2 N, 0.4 N, 0.8 N, and 1.2 N, as taken from Table XI, all six points are seen to occupy positions

Curves show relation between the Ion-fractions of the metals and the Mol-fractions of the salts at a fixed Total Salt Concentration.





in harmony with the same conclusion.

(6) Calculation of the change of the degree of dissociation of the amalgams with change of concentration;- From the data given in Table I and the formula $Me_n = \frac{y_n}{y_1}$, developed in the theoretical part, the change in the degree of dissociation of each amalgam in the mixture with changing concentration may now be calculated.

The results of these calculations, derived from mean values only, are given in Table XIII, in which the first column refers numerically to the experiments in Table I from which the calculations are made, columns two and three to the concentration of the amalgam with respect to each metal in terms of milli-equivalents per 10 grams of mercury, column four to the concentration of the amalgam in total milli-equivalents of metals per 10 grams of mercury, columns five and six to the calculated concentration of the free atoms of each metal in the amalgam at successive dilutions, based on the assumption that the concentration of these atoms is in the case of each metal equal to unity in the most concentrated amalgam.

Table XIII

Nos. of Exps. in Table I.	Concentration in milli-equivalents of each metal per 10 grams of mercury		Concentration in total milli-equivalents of metals per 10 grams of Hg.	Concentration in	
	Na	Sr		Na	Sr
1 - 22	.317	1.043	1.360	1.00	1.00
23 - 34	.242	.505	.747	.763	.485
35 - 46	.156	.239	.395	.492	.232
47 - 64	.102	.102	.204	.320	.0974
65 - 70	.0562	.0302	.0864	.177	.0289
71 - 76	.0303	.0105	.0408	.0956	.0101

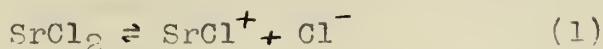
From these results it is readily seen that the increase of association upon dilution with mercury is much more pronounced in the case of the strontium amalgam than in that of the sodium amalgam.

V. DISCUSSION.

This investigation has shown that in equivalent mixtures of sodium and strontium chlorides the ion-fraction of the strontium decreases, while the ion-fraction of the sodium increases correspondingly, with increasing total salt concentration. This holds true up to about 1.6 N, above which the ion-fractions remain constant. While we are able by means of the data obtained to calculate the ion-fractions of the two metals, these data nevertheless do not enable us to calculate the actual concentration of the ions in the mixed solution.

The ion-fraction changes above referred to may be due to one or more of the following causes: (a) the existence of intermediate ions, (b) the formation of complexes in the solution, (c) the hydration of the ions, etc.

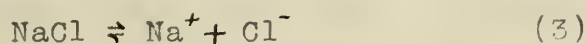
(a) There no longer seems to be a question as to the existence of intermediate ions in solutions of tri-ionic salts. On this basis strontium chloride would first ionize as follows,



and the SrCl^+ ion would again ionize to give the simple Sr^{++} ion,

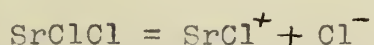


With the sodium chloride only one simple form of ionization is possible,



From these three equations it may be seen that in equivalent mixtures, according to the mass law, the common Cl^- ion should decrease the concentration of the simple Sr^{++} ion much more rapidly than that of the Na^+ ion.

Noyes and Falk (2) have shown great differences in the results concerning the degree of ionization of salts depending upon whether the calculations are made from conductance or from freezing point data. They found the greatest differences in the case of the bi-valent metal halides, where with CaCl_2 and MgCl_2 , in solutions of less than normal concentration, it ranges from 3-9 %, depending upon the concentration. W. D. Harkins and H. M. Paine (13) in their study of the effect of salts on the solubility of other salts give evidence pointing to the existence of the SrCl^+ ion; they also make the following statement, " The first step in the ionization of strontium chloride is



and in very concentrated solutions this should be almost the only form of ionization." This of course would mean that the concentration of the simple Sr^{++} ions in such a solution is very small. While the present work gives no evidence of the actual concentrations of the ions in the solution, an exceedingly rough comparison may nevertheless be based upon it. In solutions of 1.6 N or above it has been shown that the ion-fractions are 0.95 Na^+ : 0.05 Sr^{++} , and since, according to conductivity methods, sodium chloride is approximately 70 % ionized at 1.6 N concentration, it follows that, on the assumption of the isohydric principle, an approximate Sr^{++} ion concentration of 0.05 - 0.06 N exists in an equivalent mixture of sodium and strontium chlorides of the above concentration. This is in good agreement with the conclusions of Harkins and Paine.

(b) Jones and Knight (14), Foote and Levy (15), Sudhaus (16), Sandonnini (6), Rudorff (17), Jamieson (19) and many others have furnished proof of the existence of complex salts. Aside from these may be mentioned the more familiar instances of K_2PtCl_6 , K_2HgI_4 , $2KCl.MgCl_2.6H_2O$ and $(NH_4)_2HgCl_4$.

Jones and Ota (19) have shown that the data obtained by conductivity and freezing point lowering, which they take as evidence of complexes in the solution, point towards a decrease in the concentration of such complexes with the dilution of the solution, thus showing that the complexes are dissociated into the simpler forms in more dilute solutions. Sandonnini (6) has also noted this behavior but on plotting his values he found that they did not give a curve with sharp breaks in it as might be expected at the point where a complex is formed; therefore he concludes that the complex is gradually formed or dissociated with increasing or decreasing concentration. There should be no sharp breaks in the curve if the complexes present are formed in accordance with the mass law. The data obtained in the present investigation upon changing the ratio of the mol-fractions in the solution at a fixed total salt concentration give further evidence in this direction. Also the fact that, with increasing dilution, the ion-fraction ratio of the metals in equivalent salt mixtures approaches the theoretical value for infinite dilution, is in good agreement with this view; since the gradual formation or dissociation of complexes would lead to a gradual change in the value of the ion-fraction ratio.

Even if we were to assume the formation of complexes in order to account for the results obtained, we still have no indication as to exactly what these complexes might be. Complexes such as those referred to are defined by A. Werner (20) as "Higher Order Compounds"

and are capable of ionizing in several different ways. If the simplest complex possible were formed in the case of the two salts under consideration, namely, $\text{SrCl}_2 \cdot \text{NaCl}$, then whether the formula be written $\text{Na}[\text{SrCl}_3]$ or $\text{Sr}[\text{NaCl}_3]$ this compound is capable of giving several different ions in the solution; but since the reaction with which we are concerned deals only with the simple Na^+ and Sr^{++} ions, these alone will be considered. The compound $\text{Na}[\text{SrCl}_3]$ would primarily give Na^+ and $[\text{SrCl}_3]$ ions, and the mass law would require that with increasing concentration of the solution greater amounts of this complex should be formed and that its ionization should at the same time decrease; i.e., that the Sr^{++} ion concentration in the solution should decrease more rapidly than the Na^+ ion concentration. This explanation also agrees with the experimental data, according to which the Sr^{++} ion concentration does decrease more rapidly than the Na^+ ion concentration. The second formula, $\text{Sr}[\text{NaCl}_3]$, on the other hand would give an excess of Sr^{++} ions, and therefore it is not in harmony with the experimental data obtained in this investigation.

(c) Even a third basis upon which the results might be explained is at hand, namely, the hydration of ions in solution. (21) This is another case of complex-formation, and the explanation referred to is obviously self evident.

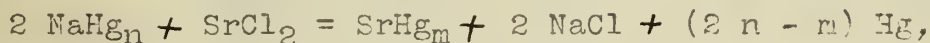
Mixed solutions are undoubtedly very complex as regards their constitution; and all of the phenomena mentioned above probably take place to some extent, and it seems hardly worth while to draw from the data at hand any specific conclusions in this direction.

VI. SUMMARY.

1. The value of the mass law expression, C_c , for the equilibrium between the mixed chloride solutions and the liquid amalgams increases directly with the concentration of the amalgam.

2. With increasing total salt concentration, at a fixed (equivalent) salt-concentration ratio, (a) the value of C_c decreases very rapidly up to about 0.8 N, after which it decreases more and more slowly until it reaches a limit at 1.6 N; (b) the ion-fraction of the sodium increases with increasing salt concentration up to about 1.6 N where it reaches a limit value of 0.95 Na^+ to 0.05 Sr^{++} .

3. With equivalent mixtures at a total concentration of 0.2 N the value of C_c increases with increase of temperature between 15° and 30°. The heat of the reaction



as determined from the Van't Hoff equation using values of C_c at 15°, 20°, 25° and 30° is about 4000 Cal.

4. In solutions of fixed total concentration the ion-fractions of the two metals vary in the direction of the mol-fraction variation of the salts in the solution but not in proportion.

5. The change in the degree of association of the metals with the dilution of the amalgams with mercury is much more rapid in the case of the strontium amalgam than in the case of the sodium amalgam.

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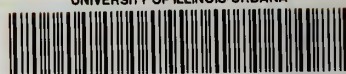
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VIII.- BIOGRAPHY.

The writer of this thesis received his early education in the public schools of Cherokee, Iowa. He entered Morningside College in 1909, was graduated with the degree of Bachelor of Arts in 1913. Entering the Graduate School of the University of Illinois in 1913 he received the degree of Master of Science in Chemistry in 1915. During the academic years 1913 - 1916 he held the position of Assistant in Chemistry in the University of Illinois and 1916 - 1917 of Fellow in Chemistry in the University of Illinois. He is a member of Phi Lambda Upsilon and author of "The Analysis of Complex Alloys of the Nickel, Copper, Chromium Type", Master's thesis at the University of Illinois.

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